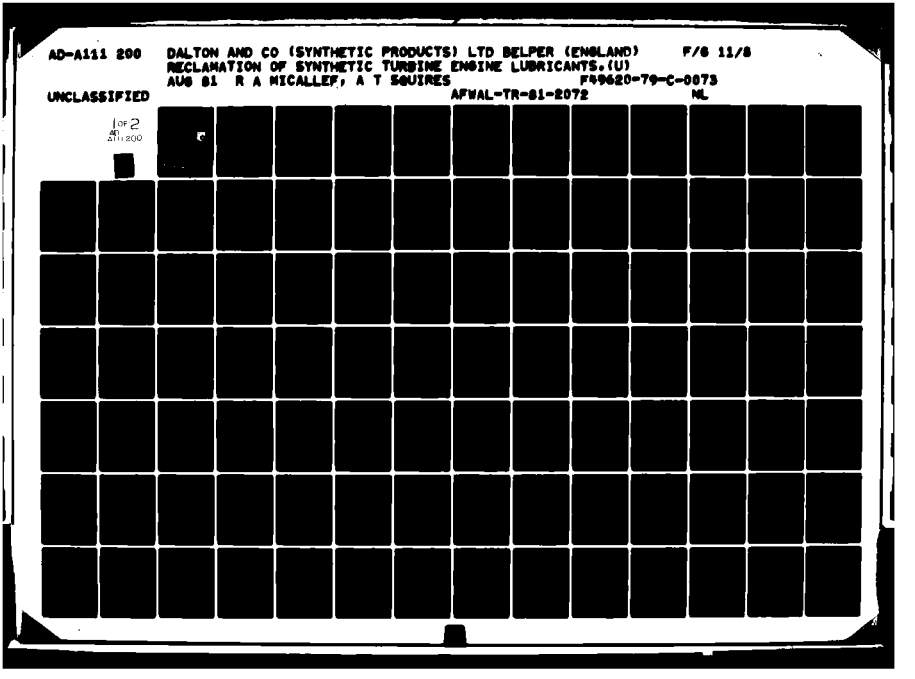
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RECLAMATION OF SYNTHETIC TURBINE ENGINE LUBRICANTS.(U)
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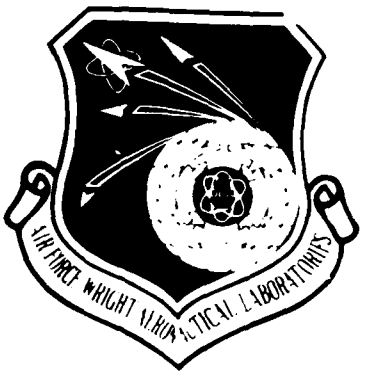
AFWAL-TR-81-2072

RECLAMATION OF SYNTHETIC TURBINE ENGINE LUBRICANTS

Dalton & Company, Ltd.
(Synthetic Products)
Silkolene Oil Refinery
Belper, Derbyshire DE5 1WT



August 1881

TECHNICAL REPORT AFWAL-TR-81-2072
Final Report for Period 1 May 1979 - 31 May 1981

AERO PROPULSION LABORATORY
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This report has been reviewed by the Office of Public Affairs (ASD/PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

HOWARD F. JONES
Project Engineer
Chief, Lubrication Branch
Fuels & Lubrication Division

FOR THE COMMANDER

ROBERT D. SHERRILL
Chief, Fuels & Lubrication Division

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1 REPORT NUMBER AFWAL-TR-81-2072	2. GOVT ACCESSION NO AD-A111 202	3 RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* RECLAMATION OF SYNTHETIC TURBINE ENGINE LUBRICANTS		5 TYPE OF REPORT & PERIOD COVERED Final Report 1 May 79 - 31 May 81 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Mr. Roger A. Micallef Mr. A.T.B.P. Squires		8. CONTRACT OR GRANT NUMBER(s) F49620-79-C-0073
9 PERFORMING ORGANIZATION NAME AND ADDRESS Dalton & Co. (Synthetic Products) Ltd. Silkolene Oil Refinery Belper, Derbyshire DE5 1WT UK		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS PE 62203F/61102F Proj/Task/WU: 3048/06/09
11. CONTROLLING OFFICE NAME AND ADDRESS Aero Propulsion Laboratory (AFWAL/POSL) Air Force Wright Aeronautical Laboratories Wright-Patterson AFB, Ohio 45433		12. REPORT DATE August 1981 13. NUMBER OF PAGES 106
14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)* EOARD/LNT Box 14 FPO New York 09510		15. SECURITY CLASS. *(of this report)* Unclassified 15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Synthetic Lubricants
Turbine Engine Lubricants
Lubricant Reclamation

20 ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Approximately 1,000 US gallons of used MIL-L-7808 lubricant arisings collected from RAF Lakenheath and RAF Upper Heyford were analyzed and reclaimed by the Dalton technology. This report covers in detail the following arising characteristics: contaminants, specific gravity, saponification, additive content, viscosity and infrared absorption spectra. Details of the proprietary Dalton technology are not disclosed, but changes in arising characteristics following reclamation are fully described. For those feedstock samples suitable for reclamation, the net yield was 95%. The reclaimed lubricant was

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analyzed in accordance with MIL-L-7808 and Rolls-Royce test procedures for corrosivity, hydrolytic stability, coking propensity and oxidative stability. A high degree of confidence is placed upon the probability of the reclaimed lubricant satisfying the requirements of the USAF.

PREFACE

This report describes the work performed by the Dalton & Company (Synthetic Products), Limited, Belper, Derby, England, under U. S. Air Force Contract F49620-79-C-0073. The report covers the period from 1 May 1979 to 31 May 1981.

This program to study "The Reclamation of Synthetic Turbine Engine Lubricants" using the Dalton-Silkolene Process was sponsored jointly by the Aero Propulsion Laboratory, Air Force Wright Aeronautical Laboratories (AFWAL/POSL), Air Force Systems Command, Wright-Patterson AFB, Ohio, and the European Office of Aerospace Research and Development, Air Force Office of Scientific Research (EOARD/LNT), Air Force Systems Command, London, England. The work was carried out under Project 3048, Task 304806, Work Unit 30480609. Project Engineers for this effort were Lt Col R. F. Felton and Lt Col W. K. Pendleton, EOARD, and Mr. H. F. Jones, AFWAL/POSL. Work was conducted at the Dalton & Company, Silkolene Oil Refinery, Belper, Derby, under the direction of Mr. R. A. Micallef and Mr. A. T. B. P. Squires, the two principal investigators for this program.

SUMMARY

Dalton & Company (S.P.) Limited, have been reclaiming, since 1956, used arisings of 7.5 cSt diester, 3 cSt diester and 5 cSt polyol ester types of turbine engine lubricant for re-use by Operators of Rolls Royce gas turbines.

An account is presented of research carried out which had the objective of reclaiming, by the Dalton technology, approximately one thousand US gallons of USAF turbine engine lubricant arisings, for evaluation by the USAF of conformity of the reclaimed material with MIL-L-7808 covering the USAF requirements for new 3 cSt viscosity turbine engine lubricant.

Earlier lubricants formulated to meet this specification were based upon diesters, but later formulations were based upon polyol esters. Results are presented of tests carried out on six different formulations of new lubricant purported to comply with MIL-L-7808. Two of these were found to fail in respect of total acid number.

The used lubricant arisings were collected from USAF aircraft based at Lakenheath and Upper Heyford in the UK. Forty five barrels of arisings were collected in all, five of which were screened out by preliminary inspection as unsuitable for reclamation. Three of these were excessively contaminated with kerosene, one with mineral lubricant and the other with a phosphate ester hydraulic fluid.

The preliminary inspection results are presented. These embraced odour, appearance, viscosity, specific gravity, saponification value, kerosene and mineral lubricant contamination, and contamination by a specific type of hydraulic fluid as revealed by TLC.

Laboratory pilot plant tests and GLC examination were carried out on samples from two barrels which exhibited contentiously low inspection results due to an unknown contaminant. It is shown that the contaminant was sufficiently volatile to be removable by the reclamation technology with consequent restoration of normal inspection results.

The repeatability of preliminary inspection was investigated with samples taken over a period of three months from two barrels of arisings. The results and calculated statistics are presented.

Thirty two of the non-rejected barrels were segregated as the feedstock (1650 US gallons) for reclamation, and the remaining eight were utilised in flushing out remnants of other lubicants in the plant. Division in this respect was entirely fortuitous, depending only upon convenience in handling and inspecting the barrels at different delivery dates.

Each barrel of the feedstock was examined by infra red spectroscopy. All the spectra exhibited large absorbance in the region of the $>C=O$ stretching band @ 1740 cm^{-1}, the main differences observed among the spectra being the relative absorbance corresponding to the asymmetric CH_2/CH_3 group ratio as influenced by base stock type, i.e. diester and/or polyol ester. It was not possible to deduce diester/polyol ester ratio from the spectra, but it is shown that the ratio of the two types of ester in a binary mixture can be obtained from such data when the nature of the component esters are known.

A first approximation of base-stock type was obtained from consideration of specific gravity and saponification value in the light of a classification which is presented. Twenty barrels of the feedstock were concluded to contain diester and polyol ester lubricants, with no great predominance of one type over the other. Five barrels were concluded to contain predominantly diester lubricants, and the remaining seven barrels to contain predominantly polyol ester lubricants.

Combined chlorine in non-ionic form was detected, either as traces or in small, but significant amounts, in all the used lubricant arisings. The chlorine-containing material was not identified, but was confirmed to be sufficiently involatile to remain in the reclaimed lubricant. Chlorine in the form of an approved additive is in general acceptable in reclaimed lubricant, but chlorine-containing contaminants are contentious in view of their possible corrosive action in a gas turbine engine environment.

Traces of combined chlorine were found in the unused lubricants excepting TEL.0029 which was found to contain 0.245% chlorine, presumably as part of a load-carrying additive.

The barrels of arisings allocated for feedstock were divided into two lots, comprising thirteen barrels of relatively low, and nineteen barrels of relatively high chlorine contents. Each lot was then blended to provide batch 1 and batch 2 of feedstock, the respective chlorine contents of which were of the order of 0.02 and 0.11%.

Proprietary details of the Dalton reclamation technology are not disclosed but, based upon this technology, a schematic illustration is given of the scheme which was adopted as most suitable for the USAF arisings. This consisted of four processing steps, the last comprising additive treatment. The two batches of feedstock were processed separately through the first three steps of the scheme. Yields from the first step, comprising vacuum-steam stripping of volatile contaminants, amounted to 95 and 96% of feedstock depending upon the degree of contamination.

Test data are presented showing the changes in properties brought about by the three processing steps. The processed batches were excessively corrosive toward copper-rich metallics, particularly in the case of the higher chlorine content batch 2 which was more corrosive than any one of the unused lubricants inclusive of the high chlorine content lubricant TEL 0029.

The corrosiveness of these batches was established to be due, not to the presence of chlorine, but to deficiencies in inhibitor contents, and it is shown that upon increasing their inhibitor contents to the levels of an inhibitor system designated HS1, details of which are given, their corrosive action was reduced below that of any of the unused lubricants. It is concluded from these results that the chlorine found in the used lubricant was in all probability derived from remnants of a load-carrying additive rather than from adventitous contamination of the consignments.

The whole of processed batch 2 and part of processed batch 1 were blended together to produce one thousand US gallons of material designated Bland 1 containing 90% and 10% of processed batches 2 and 1 respectively. The reason for utilising the whole of the higher chlorine content batch 2 in this way was to extend experience in the application of the technology to used lubricant containing non-removable chlorine compounds.

The final step of the technology viz., additive treatment, was applied to Blend 1 to produce the finished reclaimed lubricant designated Blend 1/AT. The treatment comprised raising the inhibitor contents of the blend to the levels of system HS1 followed by incorporation of 0.5% of a load-carrying agent to ensure satisfactory gear performance.

Inhibitor contents of the used lubricant arisings, feedstock batches, processed batches and the final reclaimed lubricant are presented. There were determined by HPLC under conditions which are presented for 4,4'-dioctyldiphenylamine; phenothiazine; 3,7-dioctylphenothiazine; N-allyl-3,7-dioctylphenothiazine; N-benzyl-3,7-dioctylphenothiazine; phenyl-1-naphthylamine; N-4-octylphenyl-1-naphthylamine; benzotriazole and anthranilamide (2-aminobenzamide).

1,4-dihydroxyanthraquinone was determined in accordance with a procedure based upon visible spectroscopy which was developed for this purpose, the details of which are given.

Two methods for determination of total acid number are compared, one of which was found to include benzotriazole with total acid number. It is shown that results furnished by either method are unaffected by the other inhibitors in system HS1.

The yield of reclaimed lubricant was 95% of feedstock or 97% of vacuum-steam stripped feedstock.

1,4-dihydroxyanthraquinone present in the feedstock was lost during the processing, but no other inhibitors in the feedstock were lost, nor were any losses incurred in the phosphorus and chlorine contents of the feedstock.

The cost of feedstock inhibitors retained during processing amounted to 37% of the cost of total inhibitors in the reclaimed lubricant (Blend 1/AT), and represented a saving of Ø659* per 1000 US gallons lubricant.

Subject to the validity of certain assumptions concerning the load-carrying agent, the cost of total additives retained from the feedstock was of the order of 41% of the cost of total additives in the reclaimed lubricant, this representing a saving of about Ø844* per 1000 US gallons lubricant.

The reclaimed lubricant was assessed by laboratory glassware tests, some of which were in accordance with MIL-L-7808, while others comprised Rolls Royce test procedures for corrosivity, hydrolytic stability, coking propensity and oxidative stability. Based upon experience in interpretation of the results, which are presented, a high degree of confidence is placed upon the probability of the reclaimed lubricant satisfying the requirements of the USAF.

The order of merit in which lubricants fall in respect of their oxidative stabilities are shown, by the results presented for the unused lubricants and the reclaimed lubricant, to depend upon both temperature and the mode of degradation upon which the assessment of oxidation is based. The oxidative stabilities of the 3 cSt polyol ester lubricants decrease more rapidly with rising temperature than has been observed with 3 cSt diester and 5 cSt polyol ester lubricants.

* Exchange rate taken as £1 = Ø2.32

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LIST OF ABBREVIATIONS

USAF	United States Air Force
AFAPL	Air Force Aero Propulsion Laboratory
EOARD	European Office of Aerospace Research and Development
IR	Infra-red
TLC	Thin Layer Chromatography
HPLC	High Pressure Liquid Chromatography
GLC	Gas Liquid Chromatography
cSt	Centistokes
DODP	4,4'-Dioctyldiphenylamine
PTZ	Phenothiazine
DOPT	3,7-Dioctylphenothiazine
NADOPT	N-Allyl-3,7-Dioctylphenothiazine
B-DOPT	N-Benzyl-3,7-Dioctylphenothiazine
PAN	Phenyl-1-Naphthylamine
MOPAN	N-4-Octylphenyl-1-Naphthylamine
BTZ	Benzotriazole
QZ	1,4-Dihydroxyanthraquinone
ABA	Anthranilamide (2-Aminobenzamide)

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1. INTRODUCTION

The present report covers a research programme carried out by Dalton and Co. (Synthetic Products) Ltd., for the United States Aero Propulsion Laboratory, under Contract No. F.49620-79C-0073.

Dalton & Co. (Synthetic Products) Ltd. hereafter referred to as Dalton is the sole reclaimer of synthetic turbine engine lubricants on behalf of Rolls Royce gas turbine operators. This activity extends back to 1956 since which the reliability of the company's performance in this field is reflected by the fact that of the millions of gallons of reclaimed lubricant utilised by numerous airlines throughout the free world, by the R.A.F., and by many industrial gas turbine operators, not one has given cause for complaint.

The objective of the research was to demonstrate the feasibility of reprocessing USAF gas turbine lubricant arisings for further use in USAF aircraft turbine engines. More specifically, the objective was to convert, by means of the Dalton reclamation technology, approximately 1000 US gallons of such arisings to the quality of unused lubricant as defined by MIL-L-7808. It was realised that either the "G" or "H" version of the specification, or something in between, might be relevant according to which were appropriate for the unused lubricants from which the used arisings had emanated.

Traditionally, synthetic turbine engine lubricants are characterised in the general sense by their kinematic viscosities @ 210°F, and their base-stock ester types. The following are the main types of synthetic turbine engine lubricant which have been reclaimed by Dalton since 1956:-

7.5 cSt	Diester Lubricants
3 cSt	Diester Lubricants
5 cSt	Polyol ester Lubricants

Experience at Dalton with the 3 cSt polyol ester type lubricant pioneered by the USAF is sparse, but some exploratory work reported to the USAF in 1975 (1)* indicated that these too, after use, might be reclaimable by the Dalton technology.

1.1 Lubricant Composition

Lubricants approved against MIL-L-7808 are not necessarily identical in composition, particularly in respect of the nature and concentrations of additives. Furthermore, the introduction of a new lubricant into service does not completely phase out those previously introduced until some considerable time has elapsed, and which may be of the order of one or more years.

Used lubricant collections in general will therefore comprise mixtures of two or more lubricant compositions, and consequently may be expected to contain a greater variety of additives than those in any one lubricant.

Interpretation of inspection data obtained for used lubricant arisings is greatly facilitated when the compositions of the original unused lubricants are known. Such information, in the reclamation of used lubricant from Rolls Royce gas turbines, is obtained at Dalton by examination of samples of all the lubricants approved by Rolls Royce, a discipline which is updated as and when further lubricants are approved.

* Numbers in parenthesis denote references at end of report.

TABLE I

Unused Lubricants

Code	Base-Stock Type
ATL 9100	Polyol Ester
ATL 9101	Diester
ATL 9102	Polyol/Diester Blend
TEL 0026	Diester
TEL 0027	Polyol Ester
TEL 0028	Polyol Ester
TEL 0029	Polyol Ester

A background of this kind had not for obvious reasons been established by Dalton in the case of USAF approved lubricants, but samples of some unused lubricants, coded as shown in Table I, were supplied by AFAPL for the purpose of acquainting Dalton with the kinds of lubricant involved.

2. DALTON RECLAMATION TECHNOLOGY

It would not be in order, under the terms of the contract, to disclose proprietary details of the Dalton reclamation technology. Suffice it to say however that the process involves three main steps apart from the final operation of additive treatment. The order and operational details of these steps can be varied in achieving optimum results with different feedstocks or in meeting the requirements of different specifications.

The scheme considered most suitable for the USAF arisings is outlined schematically in FIG. 1 which shows also the designations used in identifying the process status of a batch of feedstock.

The term consignment in this scheme denotes the used lubricant content of an individual vessel, regardless of size. For example, tankers, barrels and smaller containers of used lubricant collections are each labelled with an individual consignment number immediately upon arrival at the Dalton plant, and a record is kept of the inspection tests carried out on each consignment. The term Batch denotes a blend of consignments before processing, and at any stage in the processing of the whole of that blend.

The designations indicating batch process status are defined more precisely in Table II.

3. USED LUBRICANT CONSIGNMENTS

The reclamation exercise was performed with lubricant arisings from USAF aircraft based at Lakenheath and Upper Heyford in the UK. These arisings were collected in barrels by the USAF, and transported by Dalton to the reclamation facility at Belper in Derbyshire where each barrel was firstly labelled with a consignment number.

All the lubricant was not available at the same time, and was transported to Belper in four lots as and when each lot of barrels became available. These are summarised, with the consignment numbers, in Table III which shows also the number of barrels that were subsequently rejected by inspection as unreclaimable.

Discontinuities in the consignment numbers are due to allocation of the missing numbers to consignments of commercial lubricant arisings which arrived between each USAF lot.

The reclamation was carried out on lots 1, 2 and 3, the reclaimable consignments of which totalled about 1650 US gallons.

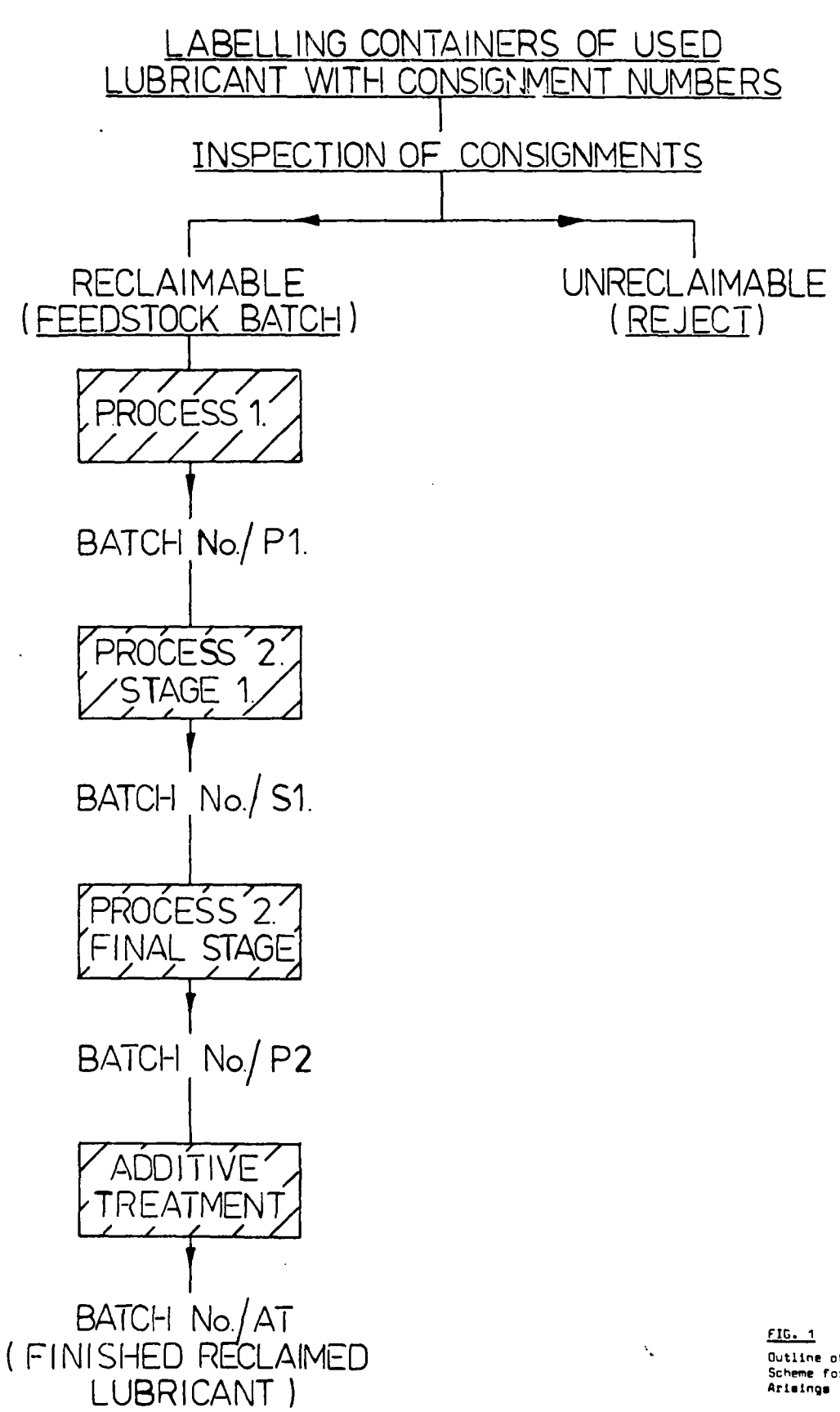


FIG. 1

Outline of Reclamation Scheme for U.S.A.F. Arisings

TABLE II

Definitions of Batch
Process Status Designations

Batch No./P1	Completion of Process 1
Batch No./S1	Completion of Process 1 and Stage 1 of Process 2
Batch No./P2	Completion of Process 1 and Process 2
Batch No./AT	Completion of Additive Treatment of Processed 2 Material

TABLE III

Summary of Lubricant Consignments - Lots 1 to 4

Number of Barrels	Origin	Consignment Nos.
	Lot 1	
1	Lakenheath	D363
21	Upper Heyford	D375 thru to D395
		Barrels Rejected = 4
	Lot 2	
8	Lakenheath	D470 thru to D477
		Barrels Rejected = None
	Lot 3	
7	Upper Heyford	D555 thru to D561
		Barrels Rejected = 1
	Lot 4	
8	Lakenheath	D587 thru to D561
		Barrels Rejected = None

With regard to lot 4 consignments, D587 and D588 were employed in a repeatability investigation (Appendix I) of certain preliminary inspection tests, and the remainder were utilised in flushing out Process 1 plant immediately prior to processing the first three lots of consignments.

3.1 Sampling and Inspection

Each sample of consignment for inspection was taken from a thoroughly shaken blend of three 400 ml aliquots, one taken from the top, one half-way down and the other near the bottom of the up-ended barrel immediately after rolling the latter and up-ending it several times.

The samples were firstly examined for odour and appearance, and then more objectively by tests employed at Dalton in screening out consignments which these preliminary tests revealed, against a background of experience, to be either unreclaimable, or uneconomically reclaimable, by the established technology.

3.2 Preliminary Inspection Results

Considering lot 1 in Table III, the four rejected consignments smelt strongly of kerosene, and were obviously less viscous than MIL-L-7808 type lubricant as seen in Table IVA for D.377, D.383, D.386 and D.390.

Referring to Table IVB, D.377, D.383 and D.386 were found to contain over 75% kerosene, while D.390 contained about 10% kerosene and 30% mineral oil.

It should be mentioned that lot 1 consignments were collected in used barrels that happened to be available on site, residuals of the previous contents of those in which the rejected consignments were collected probably being responsible for the excessive contamination observed. It is noted in Table IVA that D.390 for example, had been collected in a barrel marked 10W/40 lube oil.

Consignment lots 2, 3 and 4 were collected in clean barrels supplied by Dalton for the purpose.

Considering lot 2 consignments, none of which was rejected, Table VA records their odours and appearances, and the preliminary inspection test results are shown in Table VB.

D.471 and D.473 were provisionally regarded as contentious in view of their rather low viscosities, saponification values and specific gravities. They were therefore subjected to laboratory pilot plant tests to determine whether or not the low results were due to contaminants sufficiently volatile to be eliminated by vacuum-steam stripping which is employed in Process 1 of the reclamation technology.

The results, shown in Table VI demonstrate the effectiveness of Process 1 in having restored to typical values the low results obtained prior to processing. The contaminant(s) responsible for the low results evidently consisted of relatively high volatility material, confirmation of which was obtained by GLC analysis as shown in Figs. 2 and 3. The peaks below 230^{0}C, produced by the more volatile material, disappeared after the application of Process 1, and D.471 and D.473 were therefore transferred to the non-rejected consignments of lot 2. The GLC analysis was performed under the experimental conditions in Appendix II.

TABLE IVA

Lot 1 Consignments - Odour and Appearance

Consignment Reference	Origin	Approx. Consignment Size in U.S. Gls.	Odour	Appearance	Previous Content of Drum (according to legible marks)
D 363	Lakenheath	45	Kerosine	O.K.	Petroleum Base Turbine Engine Oil
D 375	Upper Heyford	50	Solvent Cellulose Thinner	Wet & Dirty	Petroleum Base Turbine Engine Oil
D 376	" "	50	Kerosine	O.K.	No legible marks
D 377	" "	50	Mainly Kerosine	Thin	Alcohol
D 378	" "	55	O.K.	O.K.	No legible marks
D 379	" "	50	O.K.	O.K.	Dry Cleaning Solvent
D 380	" "	50	O.K.	Wet	No legible marks
D 381	" "	55	O.K.	Wet	No legible marks
D 382	" "	50	O.K.	Wet	No legible marks
D 383	" "	45	Mainly Kerosine	Thin	No legible marks
D 384	" "	40	O.K.	Wet & Dirty	10W/40 Lube Oil
D 385	" "	45	O.K.	Wet	Dry Cleaning Solvent
D 386	" "	45	Mainly Kerosine	Thin	No legible marks
D 387	" "	50	O.K.	Wet	Petroleum Base Turbine Engine Oil
D 388	" "	45	O.K.	O.K.	Alcohol
D 389	" "	45	O.K.	Wet & Dirty	No legible marks
D 390	" "	50	Kerosine	Dirty & Thin	10W/40 Lube Oil
D 391	" "	45	O.K.	O.K.	No legible marks
D 392	" "	50	O.K.	O.K.	Petroleum Base Turbine Engine Oil
D 393	" "	50	Slight Solvent	Wet & Dirty	Petroleum Base Turbine Engine Oil
D 394	" "	50	O.K.	O.K.	No legible marks
D 395	" "	50	O.K.	O.K.	No legible marks

TABLE IVB

Lot 1 Consignments - Preliminary Inspection Tests

Ref. No.	Kinematic Viscosity - cS. 100°F.	Kinematic Viscosity - cS. 210°F.	S.G. @ 60°F/60°F.	Acidity - mgKOH/g. -	Sap. Value - mgKOH/g. -	Mineral Oil %	Kerosine %	Phosphate Ester Hyd. Fluid	Remarks
D 383	3.04	11.3	0.933	0.44	282	< 0.5	Approx. 10	Nil	Pass
D 375	3.42	13.7	0.947	0.39	310	< 0.5	< 2	Nil	Pass
D 376	2.58	8.9	0.918	0.36	237	< 0.5	Approx. 10	Nil	Pass
D 377							> 75	Nil	Reject
D 378	3.45	13.8	0.951	0.40	322	< 0.5	< 2	Nil	Pass
D 379	3.43	13.7	0.950	0.44	321	< 0.5	< 2	Nil	Pass
D 380	3.37	13.4	0.949	0.37	318	< 0.5	< 2	Nil	Pass
D 381	3.35	13.4	0.944	0.41	301	< 0.5	< 2	Nil	Pass
D 382	3.32	13.1	0.945	0.46	310	< 0.5	< 2	Nil	Pass
D 383							> 75		Reject
D 384	3.21	13.6	0.940	0.47	295	< 0.5	< 2	Nil	Pass
D 385	3.39	13.3	0.944	0.50	306	< 0.5	< 2	Nil	Pass
D 386							> 75		Reject
D 387	3.39	13.4	0.945	0.46	309	< 0.5	< 2	Nil	Pass
D 388	3.42	13.4	0.945	0.48	310	< 0.5	< 2	Nil	Pass
D 389	3.35	13.3	0.945	0.51	309	< 0.5	< 2	Nil	Pass
D 390	2.23	7.2	0.891	0.28	155	30	Approx. 10	Nil	Reject
D 391	3.31	13.2	0.942	0.53	295	< 0.5	< 2	Nil	Pass
D 392	3.24	12.7	0.940	0.58	288	< 0.5	< 2	Nil	Pass
D 393	3.39	13.6	0.942	0.43	292	< 0.5	< 2	Nil	Pass
D 394	3,35	13.3	0.942	0.67	294	< 0.5	< 2	Nil	Pass
D 395	3.27	12.9	0.941	0.58	298	< 0.5	< 2	Nil	Pass

TABLE VA

Lot 2 Consignments - Odour and Appearance

Consignment Reference	Origin	Approx. Consignment Size in U.S. Gins.	Odour	Appearance	Previous Content of Drum
D 470	Lakenheath	50	O.K.	Wet	Clean barrels, painted white with brown band, supplied by Dalton & Co. (S.P.) Ltd. for collection of these consignments
D 471	"	50	O.K.	O.K.	
D 472	"	50	O.K.	O.K.	
D 473	"	40	O.K.	O.K.	
D 474	"	40	O.K.	O.K.	
D 475	"	45	O.K.	O.K.	
D 476	"	55	O.K.	Wet & Dirty	
D 477	"	45	Slight Solvent	O.K.	

TABLE VB

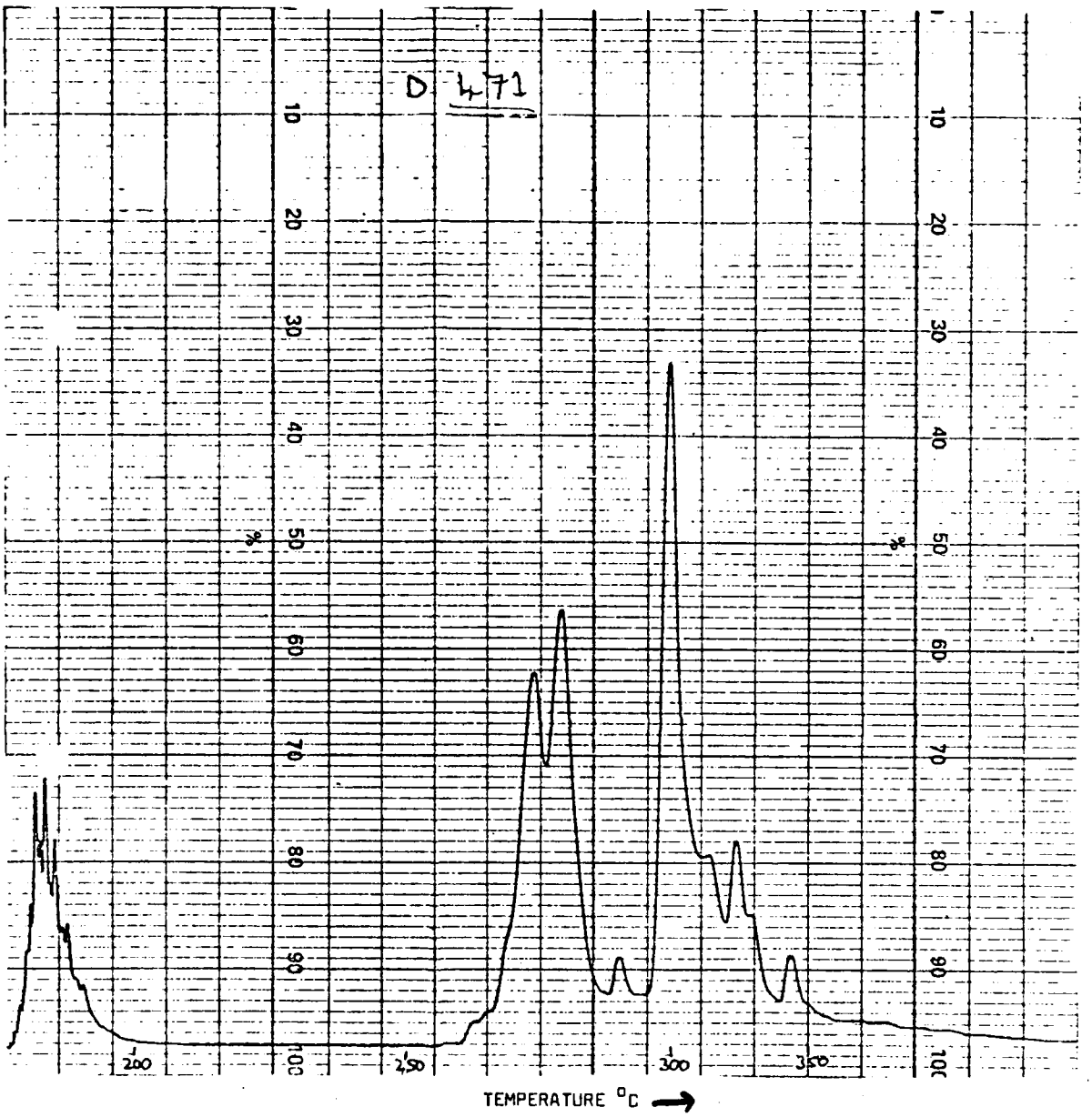
Lot 2 Consignments - Preliminary Inspection Tests

Ref. No.	Kinematic Viscosity - cS. 100°F.	Kinematic Viscosity - cS. 210°F.	S.G. @ 60°F/60°F.	Acidity - mgKOH/g. -	Sap. Value - mgKOH/g. -	Mineral Oil %	Kerosine %	Phosphate Ester Hydraulic fluid	Remarks
D 470	13.1	3.34	0.936	0.52	285	<0.5	<2	NIL	PASS
D 471	10.5	2.90	0.926	1.04	271	<0.5	<2	NIL	?
D 472	13.4	3.40	0.940	0.52	293	<0.5	<2	NIL	PASS
D 473	10.8	2.95	0.931	0.62	276	<0.5	<2	NIL	?
D 474	11.8	3.14	0.932	0.76	278	<0.5	<2	NIL	PASS
D 475	12.9	3.32	0.937	0.58	288	<0.5	<2	NIL	PASS
D 476	13.0	3.30	0.936	0.70	282	<0.5	<2	NIL	PASS
D 477	11.1	3.01	0.930	0.74	278	<0.5	<2	NIL	PASS

TABLE VI

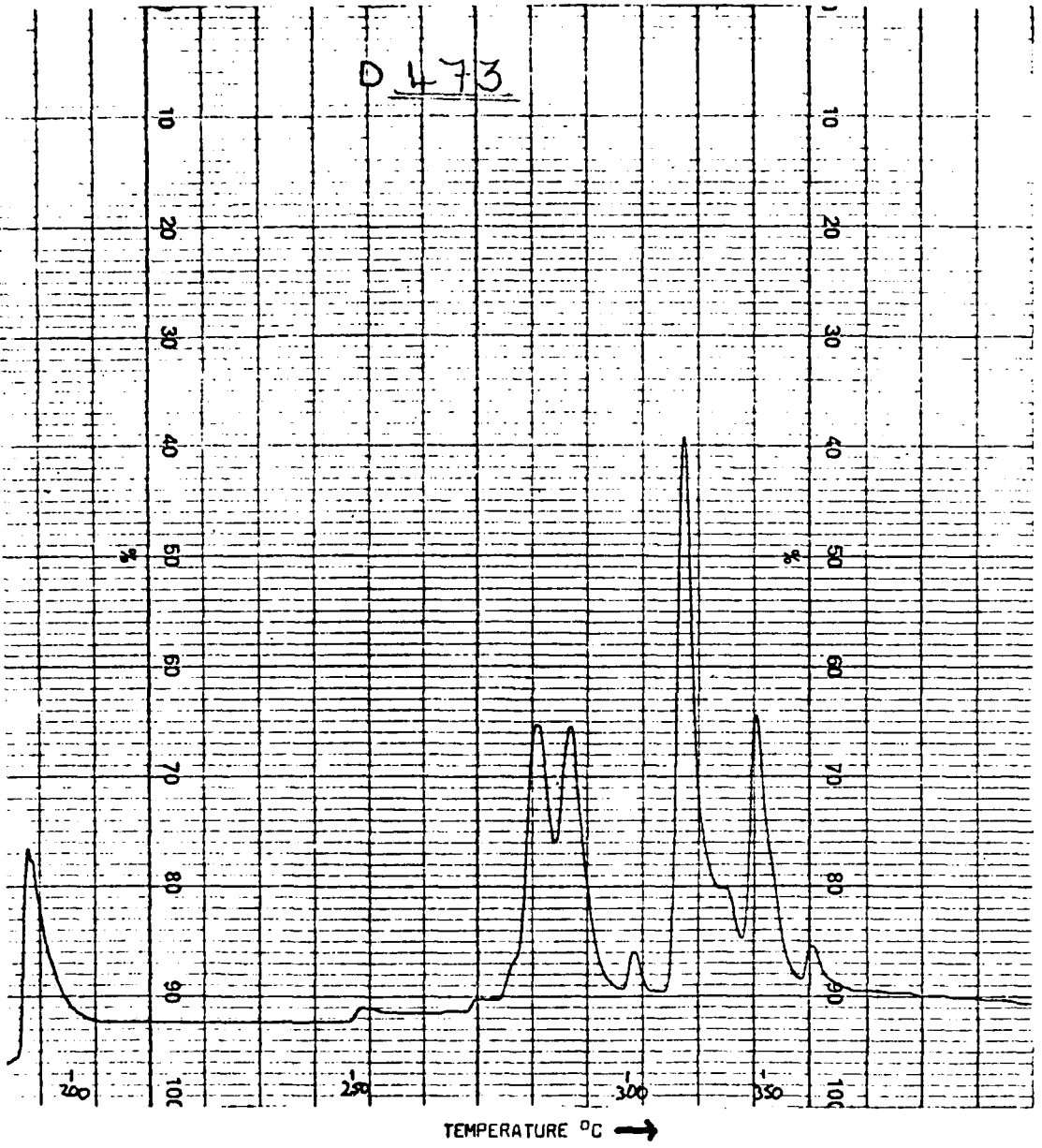
Effect of Process 1
on
Contentious Consignments
D471 and D473

	D.471		D.473	
	Before Process	After Process	Before Process	After Process
Specific Gravity $60^{o}F/60^{o}F$	0.926	0.941	0.931	0.940
Saponification Value mgKOH/g	271	294	276	293
Kinematic Viscosity @ $210^{o}F$ - cSt	2.90	3.38	2.95	3.39
Kinematic Viscosity @ $100^{o}F$ - cSt	10.5	13.1	10.8	13.2
TAN - mgKOH/g	1.04	0.64	0.62	0.48



Gas Chromatogram - Consignment D.471

FIG. 2



Gas Chromatogram - Consignment D.473

FIG. 3

It is pertinent at this juncture to refer again to Table VB in which it is seen that the viscosities @ 210°F of D.471 and D.473, which preliminary inspection indicated to be contentious, were a little below the MIL-L-7808 requirement of 3.0 cSt minimum. On the other hand, it is seen that the viscosity of D.477, which was not regarded as contentious, was only 0.01 cSt above the specification minimum, and this raised the question of what confidence could be placed upon the decision to pass this consignment through preliminary inspection.

An investigation into the repeatability of preliminary inspection was therefore carried out on D.587 and D.588 from lot 4 consignments, the results of which are given in Appendix I ; the reason for selecting these particular consignments was to avoid interference with the reclamation of the thirty two drums of the non-rejected consignments of lots 1, 2 and 3.

Considering lot 3 consignments, one of which was rejected, Table VIIA records their odours and appearances. These consignments were very much better in appearance than lots 1 and 2, their colours and clarities suggesting that they had suffered less degradation during use. It is of interest to note from the preliminary inspection test results shown in Table VIIB that their specific gravities and saponification values were in general higher than the results previously shown for lots 1 and 2, this suggesting a predominance of polyol ester base stock as will be illustrated later.

With regard to the rejected consignment D.555, this was found by TLC to be contaminated with a phosphate ester type of hydraulic fluid, the origin of which was a mystery. Concern over its presence stems from early experience at Rolls Royce when it was found that contamination by such material of lubricant exposed to high bearing compartment temperatures could lead to the corrosion pitting of rolling contact bearings.

The non-rejected consignments of lots 1, 2 and 3 were next examined in respect of infra-red spectra, base-stock type, inhibitor contents and finally, chlorine level.

3.3 Infra-red Spectra

The infra-red spectra obtained for all the consignments were similar apart from differences in the aliphatic C-H stretching bands @ 2800 - 3000 cm^{-1}.

Each one of the spectra exhibited large absorbance in the region of the $>C=O$ stretching band @ 1740 cm^{-1}, this confirming the consignments to be comprised substantially of esters in accord with expectations from their histories.

With regard to the aliphatic C-H stretching bands @ 2800 - 3000 cm^{-1}, these consisted of four peaks as follows:-

CH_3 Asymmetric stretch @ 2960 cm^{-1}

CH_2 Asymmetric stretch @ 2930 cm^{-1}

CH_3 Symmetric stretch @ 2870 cm^{-1}

CH_2 Symmetric stretch @ 2860 cm^{-1}

TABLE VIIA

Lot 3 Consignments - Odour and Appearance

Consignment Reference	Origin	Approx. Consignment Size in U.S. Gls.	Odour	Appearance	Previous Content of Drum
D.555	Upper Heyford	40	O.K.	O.K.	Clean barrels, painted white with brown band, supplied by Dalton & Co. (S.P.) Ltd. for collection of these consignments.
D.556	"	45	O.K.	O.K.	
D.557	"	50	O.K.	O.K.	
D.558	"	50	O.K.	O.K.	
D.559	"	50	O.K.	O.K.	
D.560	"	45	O.K.	O.K.	
D.561	"	45	O.K.	O. .	

TABLE VIIB

Lot 3 Consignments - Preliminary Inspection Tests

Ref. No.	Kinematic Viscosity - cS. 100°F.	Kinematic Viscosity - cS. 210°F.	S.G. @ 60°F/60°F.	Acidity - mgKOH/g. -	Sap. Value - mgKOH/g. -	Mineral Oil %	Kerosine %	Phosphate Ester Hydraulic fluid %	Remarks
D.555	13.6	3.34	0.953	0.22	325	<0.5	<2	0.3	REJECT
D.556	13.7	3.43	0.952	0.34	316	<0.5	<2	NIL	PASS
D.557	13.3	3.39	0.952	0.57	318	<0.5	<2	NIL	PASS
D.558	13.6	3.36	0.952	0.33	320	<0.5	<2	NIL	PASS
D.559	13.4	3.38	0.953	0.44	324	<0.5	<2	NIL	PASS
D.560	13.9	3.35	0.956	0.20	324	<0.5	<2	NIL	PASS
D.561	13.7	3.37	0.954	0.47	321	<0.5	<2	NIL	PASS

The main differences noted here among the spectra was the relative absorbance corresponding to the asymmetric CH_2/CH_3 group ratio. These differences were interpreted, from theoretical considerations, and spectra obtained for the unused lubricants ATL.9100 and ATL.9101, to be due to differences in the proportions and types of diester and polyol ester base-stocks present. (Appendix III).

3.4 Base-Stock Type

Detailed knowledge of the base-stock compositions of the consignments, which might have been gained via GLC analysis for example, was not essential in so far as the objective of the research was concerned. Instead, an approximate indication of base-stock type was obtained from consideration of specific gravity and saponification value in the light of the classification shown in Table VIII.

This classification is based upon test data accumulated by Dalton in the reclamation of numerous 3 cSt diester and 5 cSt polyol ester lubricants, including a few 3 cSt polyol ester lubricants.

It was recognised that some MIL-L-7808 polyol ester lubricants, outside the range of Dalton's sparse experience with these, might not fit the classification, but it was conjectured that the deviations would not be all that great.

Results obtained for the unused lubricant samples are shown in Table IX, from which it is seen that whereas they fit the classification in respect of specific gravity, the saponification values for TEL.0027 and TEL.0028 fall a little below the 320 minimum assigned in the classification to polyol ester lubricants. Concordance between the two criteria of assessment would be reached if the 320 minimum were lowered to 315 which would thus appear to be the more realistic.

Examples of polyol esters having saponification values below 320 are neopentyl and dipentyl glycols esterified with aliphatic acids having carbon numbers of eight or more.

The non-rejected consignments of lots 1, 2 and 3 are grouped by the classification as shown in Table X.

The proportions of each lot falling into the three groups defined by saponification value are seen, in the case of lots 1 and 3, to be not in entire agreement with those falling in the same groups defined by specific gravity. A study of the saponification values shows however that here again the discrepancies disappear when the classification minimum of 320 for polyester lubricants is amended to 315.

Despite the discrepancies, the following references may be drawn from Table X:-

(a) Almost the whole of lot 1 consignments comprised diester/polyol ester mixtures.

(b) Half of lot 2 consignments comprised diester/polyol ester mixtures, while the other half was predominantly rich in diesters.

(c) The whole of lot 3 consignments was predominantly rich in polyol esters.

TABLE VIII

Base-Stock Type Interpretation
of
Specific Gravity
and
Saponification Value

Specific Gravity $60^{o}F/60^{o}F$	Inference
Below 0.935	Exclusively or Predominantly Diester
0.935 - 0.950	Mixture of Diester and Polyol Ester
Above 0.950	Exclusively or Predominantly Polyol Ester

Saponification Value mgKOH/g	Inference
Below 280	Exclusively or Predominantly Diester
280 - 320	Mixture of Diester and Polyol Ester
Above 320	Exclusively or Predominantly Polyol Ester

TABLE IX

Specific Gravities and Saponification Values
of
Unused Lubricant Samples

Unused Lubricant	Specific Gravity $60^{o}F/60^{o}F$	Saponification Value	Known Base-Stock Type
ATL 9100	0.965	338	Polyol Ester
ATL 9101	0.930	277	Diester
ATL 9102	0.941	286	Diester and Polyol Ester
TEL 0026	0.928	281	Diester
TEL 0027	0.956	319	Polyol
TEL 0028	0.951	315	Polyol
TEL 0029	0.952	324	Polyol

TABLE X

Grouping of non-rejected Consignments
of
Lots 1, 2 and 3
by
Specific Gravity and Saponification Value

		Number of Consignments		
		Lot 1	Lot 2	Lot 3
Specific Gravity $60^{o}F/60^{o}F$	Below 0.935	1	4	None
	0.935 to 0.950	16	4	None
	Above 0.950	1	None	6
Saponification Value mgKOH/g	Below 280	1	4	None
	280 to 320	15	4	2
	Above 320	2	None	4

Collecting together the results in Table X, we have the summary shown in Table XI for the 32 non-rejected consignments. Thus if these consignments were blended together, as was the original intention, the blend would consist substantially of diester and polyol ester lubricants with no great predominance of one type over the other. However, for reasons explained later, it was considered prudent, before applying the reclamation technology, to divide the consignments into two batches based upon chlorine levels.

3.5 Inhibitor Contents

Listed in Table XII are the more common oxidation and corrosion inhibitors, comprising antioxidants and metal passivators respectively, which have been found by Dalton in synthetic lubricant arisings from commercial gas turbines. The right hand column of the list gives the trivial designations which will be employed in the text for the sake of brevity.

Inhibitors determined in the non-rejected consignments of lots 1, 2 and 3 were found to range in concentration as shown in Table XIII. These, apart from quinizarin, were determined by HPLC analysis under conditions which are given in Appendix IV. Quinizarin at this stage of the research was tested for qualitatively by shaking a small sample of each consignment in a test tube with powdered calcium hydroxide, allowing the latter to settle and observing the colour from underneath. A purple colour indicates the presence of quinizarin which, as is well known, is orange-red in acidic, and purple-blue in basic media; this simple technique is particularly useful in the case of dark-coloured lubricants.

Quinizarin was found in all the consignments of lots 1 and 2, but none was found in any of those of lot 3. Lot 3 consignments were found to contain, on average, less DODP but more PAN and MOPAN than the averages of these antioxidants found in lots 1 and 2 consignments.

3.6 Chlorine

The presence of chlorine compounds in used lubricant arisings requires careful attention, especially when they are not removable by the reclamation technology, and therefore remain in the final reclaimed product.

Concern of the presence of such materials arises from the corrosive action of many chlorine compounds and their decomposition products. They could be harmful for example in the 'hot-end' bearing compartments of gas turbines, not only at elevated temperature, but also under shut-down and standby conditions when moisture condensation may be present as well.

Contamination of used lubricant arisings by compounds considerably more volatile than the base-stock components of the lubricant such as industrial chlorinated solvents for example can be dismissed since these are readily removed by vacuum-steam stripping in Process 1 of the technology.

Non-removable chlorine derived from an additive in one or more of the original lubricants from which the arisings had emanated is in general acceptable in the reclaimed lubricant, otherwise the additive would not have been approved in the first place.

TABLE XI

Summarised Base-Stock Classification
of
The 32 non-rejected Consignments
of
Lots 1, 2 and 3

Base Stock	Number of Consignments	
	Based Upon Specific Gravity	Based Upon Saponification Value
Diester	5	5
Diester/Polyol Ester	20	21
Polyol Ester	7	6

TABLE XII

Inhibitors Found by Dalton
in
Commercial Gas Turbine Lubricant Arisings

4,4'-Dioctyldiphenylamine	DODP
Phenothiazine	PTZ
3,7-Dioctylphenothiazine	DOPT
N-Allyl-3,7-Dioctylphenothiazine	NADOPT
N-Benzyl-3,7-Dioctylphenothiazine	B-DOPT
Phenyl-1-Naphthylamine	PAN
N-4-Octylphenyl-1-Naphthylamine	MOPAN
Benzotriazole	BTZ
1,4-Dihydroxyanthraquinone	QZ
Anthranilamide (2-Aminobenzamide)	ABA

TABLE XIII

Concentration Ranges of Inhibitors
Determined in non-rejected Consignments
of
Lots 1, 2 and 3

	Lot 1	Lot 2	Lot 3
DODP	0.97-1.91	1.16-1.80	0.83-1.02
PTZ	nd	nd	nf-0.003
DOPT	nf-<0.01	nf	nf-0.004
NADOPT	nf-0.09	0.03-0.09	nf-0.005
PAN	0.04-0.23	0.06-0.21	0.04-0.42
MOPAN	0.04-0.42	nf-0.05	0.2-0.52
BTZ	nd	nd	nd
QZ	Present	Present	Absent

nd - Not Determined

nf - Not Found

Apart from chlorinated biphenyls which are no longer employed in those gas turbine lubricants in which they originally featured, and which were reclaimable, all the lubricants reclaimed by Dalton over the years were free from chlorine-containing additives.

The non-rejected consignments of lots 1, 2 and 3 were tested for chlorine by fusion of 1 ml samples with sodium (Lassaigne's Test) and identification as silver chloride after expulsion of any hydrocyanic acid from the acidified water extract of the sodium salt.

Chlorine was found in all the consignments in amounts which were adjudged from the intensities of the silver chloride clouds produced. The consignments fell into one or the other of two groups based upon the adjudged chlorine levels as shown in Table XIV.

Some idea of the order of magnitude which can be assigned to the chlorine levels in each group was obtained by determining the chlorine contents of D.473 and D.560 in accordance with IP.118/65 (Joint ASTM D.1317-64) except that the sodium chloride was titrated with silver nitrate potentiometrically. The results are shown at the bottom of Table XIV.

The combined chlorine was confirmed to be non-ionic by the absence of chloride ions in dilute nitric acid extracts from samples of the consignments, and no change in the chlorine levels of D.382 and D.560 were observed after samples of these had been vacuum-steam stripped in the laboratory Process 1 pilot plant.

The possibility existed that the non-removable chlorine-containing material might be an approved load-carrying additive such as a chlorine substituted alkyl phosphate or phosphite for example. However, in the absence of positive identification of the material, tests were made for chlorine in ATL.9100, ATL.9101 and ATL.9102 which were the only three unused lubricants available at the time. The results, presented in Table XV, showed these to contain very little chlorine, far less than would be expected from the presence of a chlor-load carrying additive.

It was understood that these particular lubricants should have been free of chlorine. They were therefore examined, with consignments D.471, D.473 and D.560 by x-ray spectroscopy which was carried out on coded samples by an independent laboratory (2). The results are presented in Table XVI where those previously obtained by the other techniques are recapitulated.

Allowing for the limitations of subjective assessment, the approximate levels of chlorine adjudged from Lassaigne's test are seen to be in reasonably good agreement with the x-ray spectroscopy results which confirmed the presence of chlorine in ATL.9100 and ATL.9102.

Since the majority of lots 1, 2 and 3 consignments were richer in chlorine than the foregoing three unused lubricants, tests were carried out to determine whether the same applied to lot 4 consignments, the results of which, with other inspection data, are shown in Table XVII.

It is seen that none of these was free of chlorine, D.560 falling into group 2, and the remainder in group 1 of the chlorine classification.

TABLE XIV

Non-Rejected Consignments of Lots 1, 2 and 3
Grouped on Basis of Chlorine Level

GROUP 1	GROUP 2
Chlorine:- Little less to little more than traces.	Chlorine:- Small amounts, but significantly more than traces.
D.376 D.382 D.387 D.391 D.394 D.470 D.471 D.472 D.473 D.474 D.475 D.476 D.477	D.363 D.375 D.378 D.379 D.380 D.381 D.384 D.385 D.388 D.389 D.392 D.393 D.395 D.556 D.557 D.558 D.559 D.560 D.561
Chlorine Content (Potentiometric Titration) of:-	
D.473:-	D.560:-
0.022% 0.024% 0.021%	0.105% 0.110% 0.120%

TABLE XV

Chlorine Levels
First Three Unused Lubricant Samples

ATL 9100	Trace Chlorine (Just detectable)
ATL 9101	No chlorine detected
ATL 9102	Trace Chlorine (Just detectable)

TABLE XVI

Confirmation of Chlorine Levels
by
X-Ray Spectrascopy

Sample	Lassaigne's Test	Chlorine %	
		Potentiometric Titration	X-ray Spectroscopy
ATL.9100	Traces Chlorine (just detectable)	-	Approx. 0.003
ATL.9101	No Chlorine detected	-	Approx. 0.001
ATL.9102	Traces Chlorine (just detectable)	-	Approx. 0.001
D.471	Group 1*	-	0.015
D.473	Group 1*	0.022	0.024
D.560	Group 2*	0.112	0.130

* See Table XIV for definition of Group

TABLE XVII

Lot 4 Consignments - Preliminary Inspection Tests and Chlorine Levels

Consignment Reference	Odour	Appearance	Kinematic Viscosity @ 100°F. in cs.	Acidity	Saponification Value - mgKOH/g. -	Chlorine Level
D.587	O.K.	O.K.	12.7	0.69	284	Group 1
D.588	O.K.	O.K.	13.4	0.56	295	Group 2
D.589	O.K.	O.K.	13.3	0.62	293	Group 1
D.590	O.K.	O.K.	12.5	0.81	286	Group 1
D.591	O.K.	O.K.	12.3	0.82	289	Group 1
D.592	O.K.	O.K.	13.5	0.49	296	Group 1
D.593	O.K.	O.K.	13.2	0.61	284	Group 1
D.594	O.K.	O.K.	13.4	0.72	290	Group 1

Note: Examination of the above consignments by TLC indicated no contamination by phosphate ester hydraulic fluid.

Considering the total of 40 non-rejected consignments in all from the four lots of arisings, half of these fell into group 2, and the other half in group 1. However, as stated earlier, lot 4 consignments were utilised in flushing out Process 1 plant in readiness for reclamation of the non-rejected consignments of Lots 1, 2 and 3, the majority of which fell into group 2 of the chlorine classification as may be seen upon returning to Table XIV.

The origin of the chlorine remained unknown at this stage of the research, and left unresolved the question of whether it constituted part of an approved additive or alternatively, a low-volatility contaminant which might give rise to unsurmountable corrosion problems in the reclaimed consignments.

The decision was taken to apply the reclamation technology, up to the end of Process 2, to the two chlorine groups of consignments separately. They were therefore firstly blended in two batches, designated Batch 1 and Batch 2 comprising the low and high chlorine-level consignments respectively.

4. RECLAMATION OF USED LUBRICANT CONSIGNMENTS

The reclamation was carried out as depicted by the flow diagram in Fig. 4.

4.1 Process 1

Process 1 is essentially a vacuum-steam stripping operation carried out in plant designed to remove volatile contaminants without oxidising or thermally degrading the feedstock.

The process was carried out to produce Batch 1/P1 and Batch 2/P1 which amounted to 97 and 98% respectively of Batch 1 and Batch 2.

Inhibitor contents determined in the two batches of processed material were as shown in Table XVIII.

These inhibitor contents may be taken to be substantially the same as those of the two batches of feedstock since it is known from experience that no inhibitors are lost in Process 1.

It is seen that Batch 2/P1 contained significantly more MOPAN than Batch 1/P1. This stems from the fact that all those consignments having MOPAN contents in excess of 0.14% happened to fall into the higher chlorine group of consignments.

Both batches contained significant concentrations of DODP, Batch 1/P1 however containing more than Batch 2/P1.

The ranges in which the concentrations of these two antioxidants were found to vary among the consignments of each batch before vacuum-steam stripping are presented in Table XIX.

The acidity of each batch, before and after Process 1, and the chlorine levels of the processed batches, as ascertained by Lassaigne's test, were as shown in Table XX from which it is seen in particular that no change occurred in chlorine level.

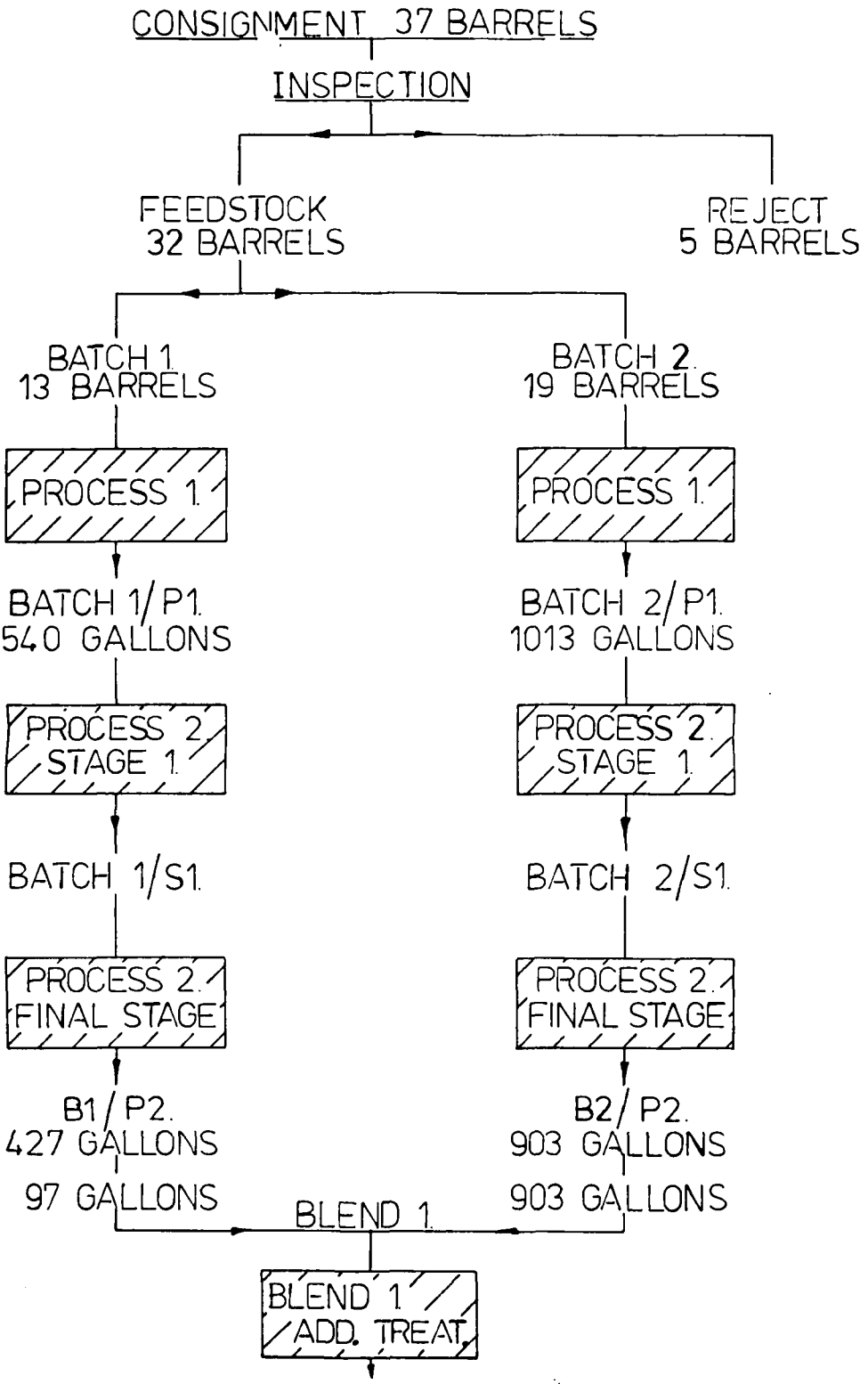


FIG 4.

REPROCESSED LUBRICANT

TABLE XVIII

Determined Inhibitor Contents
of
Batch 1/P1 and Batch 2/P1

Inhibitor	Batch 1/P1	Batch 2/P1
NADOPT %	0.03	nf
DODP %	1.30	0.94
MOPAN %	0.07	0.31
PAN %	0.14	0.12
DOPT %	nf	nf
PTZ %	nf	nf
Quinizarin	Present	Present

nf - not found

TABLE XIX

MOPAN and DODP
Concentration Ranges

Batch 1 and Batch 2
Consignments

	Batch 1 Consignments	Batch 2 Consignments
MOPAN %	Nil - 0.14	0.04 - 0.52
DODP %	1.16 - 1.91	0.82 - 1.52

TABLE XX

Effect of Process 1 on the
Acidities and Chlorine Levels
of
Batch 1 and Batch 2 Consignments

		Batch 1	Batch 2
TAN	Before Process 1	0.68	0.48
	After Process 1	0.68	0.48
Chlorine After Process 1		Traces (Group 1)	Small Amount (Group 2)

4.2 Process 2, Stage 1

The two batches of Processed 1 material were next subjected to Stage 1 of Process 2 to produce Batch 1/S1 and Batch 2/S1 as depicted in Fig. 4.

The primary function of Stage 1 of Process 2 is to lower acidity, the effectiveness of which in this respect is illustrated by the results in Table XXI.

It is seen that although a satisfactory lowering of acidity had taken place, no change occurred in chlorine level. This however would represent an asset if, as was suspected, the chlorine existed in the form of an approved additive.

4.2.1 Corrosivity - Batch 1/S1 and Batch 2/S1

Having lowered the acidities of both batches to a substantially common level, corrosion tests were carried out on Batch 1/S1 and Batch 2/S1.

The test conditions comprised pretreatment of each sample by 5 hrs/250°C confined-heating in accordance with Rolls Royce method 1004/Supp.1 followed by a 192 hrs/250°C corrosion test on each of the pretreated samples in accordance with Rolls Royce Method 1002. A summary of the test procedure is given in Appendix V.

This test procedure is intentionally somewhat severe, and was originally devised to assess the corrosiveness at engine bulk-oil temperatures of lubricant which had spent part of its life at higher temperatures in the "hot-end" bearing compartments of the gas turbine, and at shut-down when transient temperatures above normal operational temperatures may occur as a result of heat soak-back phenomenon.

The pretreatment provides an opportunity for unstable additives to decompose, and for a substantial proportion of acidic and other volatile degradation products generated by additives and/or the lubricant base-stock to contaminate the sample rather than escaping to atmosphere. The reason for carrying out the corrosion test itself at lower temperature is to minimise the formation of lacquer on the metal specimens, since this can retard corrosion rates and lead to lower and more erratic weight losses than would otherwise occur.

Corrosivity was assessed in terms of the changes in the weights of the metal test specimens, and their appearances under a magnification of ten diameters, at the end of the test.

The results are presented in Tables XXIIA and XXIIB in which are also presented the results of parallel tests carried out on three of the unused lubricants viz., ATL 9100, ATL 9101 and ATL 9102. The last column of each Table shows, for comparison, the corrosivity requirements imposed by Rolls Royce in their specifications for reclaimed gas turbine lubricants (3). The following comments are relevant to these results:-

a. Magnesium

Batch 1/S1 produced greater metal loss than Batch 2/S1, but ATL 9101 and ATL 9102 produced greater losses than Batch 1/S1. ATL 9100 was comparable with Batch 1/S1.

TABLE XXI

Effect of Stage 1 of Process 2
on the
Acidities and Chlorine Levels
of
Batch 1/S1 and Batch 2/S1

	Batch 1/S1	Batch 2/S1
TAN	0.09	0.08
Chlorine	Traces (Group 1)	Small Amount (Group 2)

TABLE XX11A

Corrosivity - 192 hours/150°C. Corrosion (R.R. 1002) After Pretreatment of Sample by 5 hours/250°C. Confined Heating (R.R. 1004/Supp. 1)

TEST SPECIMEN	Metal Weight Change in mg/cm^2					
	Batch 1/S1	Batch 2/S1	ATL9100	ATL9101	ATL9102	Rolls Royce Requirements
Magnesium Alloy	- 4.6	- 1.4	- 4.0	- 10.1	- 6.3	Report
Aluminium Alloy	<0.1	<0.1	<0.1	<0.1	<0.1	0.1 maximum
Mild Steel	<0.1	<0.1	<0.1	<0.1	<0.1	0.1 maximum
Soldered Copper	- 2.1	- 5.6	+ 0.3	- 0.3	<0.1	3.0 maximum
Lead	- 10	- 21	- 39	- 23	- 48	Report
Copper	- 0.33	- 1.0	<0.05	- 0.42	- 0.06	1.0 maximum
Brass	- 1.9	- 4.4	- 0.60	- 2.1	- 0.20	4.0 maximum

TABLE XXIIB

Corrosivity - 192 hours/150°C. Corrosion (R.R. 1002) After Pretreatment of Sample by 5 hours/250°C. Confined Heating (R.R. 1004/Supp. 1)

TEST SPECIMEN	Appearance of Specimen					
	Batch 1/S1	Batch 2/S1	ATL9100	ATL9101	ATL9102	Rolls Royce Requirements
Magnesium Alloy	$D_g(x)$	$D_g(x)$* $P_g(x)$	$D_g(m)$ $P_g(m)$	$D_g(x)$ $E_c(m)$	$D_1(m)$ $E_g(m)$	Report
Aluminium Alloy	0	0	0	0	0	No Etching or Pitting
Mild Steel	0	0	0	0	0	No Etching or Pitting
Soldered Copper	$D_g(m)$ $E_c(m)$	$D_g(x)$* $E_1(x)$	$D_g(s)$ $E_g(m)$	$D_g(s)$ $E_c(m)$	$D_g(m)$	Report
Lead	$D_g(m)$*	$D_g(m)$*	$D_g(s)$	$D_g(s)$	0	Report
Copper	$D_g(m)$ $E_1(m)$	$D_g(s)$ $E_g(m)$	$D_g(s)$	$D_g(m)$ $E_c(s)$	$D_g(m)$	Report
Brass	$D_g(m)$ $E_g(m)$	$D_g(m)$ $E_g(x)$	$D_g(m)$ $E_g(m)$	$D_1(m)$ $E_g(m)$	$D_g(m)$ $E_g(s)$	Report

Descriptive Key:- 0 = no change; D = discoloured; E = etched; P = pitted; l = local; g = general; (s) = slight; (m) = moderate; (x) = excessive; * = depositon of Copper

These differences however are really of little practical significance in view of the high oxidation potential of magnesium, and the fact that this is normally combated in practice by means of anodic and/or other surface treatments of magnesium components in gas turbine systems.

b. Lead

The high metal losses produced by all the lubricants are not abnormal, and very little importance can be attached to the differences in view of the capricious behaviour of lead under the test conditions employed.

c. Cupro Materials

The relatively high corrosiveness of Batch 2/S1 (high chlorine content) toward the cupro specimens represented a contentious feature in that the weight losses of copper and brass ordered upon the Rolls Royce limits, and that of the soldered copper was significantly greater. The cupro specimens in all the tests had undergone etching, more so however in the case of Batch 2/S1 than the other lubricants tested.

d. Aluminium and Steel

The aluminium and mild steel specimens in all the tests remained unchanged in appearance. The absence of corrosion pits in the steel specimens was of particular interest in the case of the two batches of partly processed consignments as this suggested that the unidentified chlorine compound(s) in these had withstood the 5 hrs/250°C pretreatment without decomposition. Supporting this was the absence of ionic chlorine which was confirmed by shaking lubricant remaining at the end of each test with dilute nitric acid, and testing the acidic extract with silver nitrate solution.

e. Severity of Pretreatment

The severity of the 5 hrs/250°C pretreatment is illustrated by the results in Table XXIII showing the increases in acidity produced upon subjecting fresh samples of lubricant to the pretreatment.

The difference between the results obtained for Batch 1/S1 and Batch 2/S1 would not be expected to influence their corrosivities significantly at the high levels of acidity produced by the pretreatment. It was not possible at this stage of the research to reach an unequivocal conclusion on whether or not the greater corrosiveness of Batch 2/S1 towards the cupro specimens was due directly or indirectly to the higher chlorine level of this batch, but the foregoing observations strongly suggested some other cause such as deficiencies in inhibitor contents for example.

Blend 1/AT in Table XXIII refers to a laboratory preparation of the final reclaimed lubricant which is introduced and discussed in Sections 4.6 & 4.7 of the present report. Suffice it to say here that the superior stability of this preparation, as reflected by the low acidity increase in Table XXIII, was achieved by the introduction of inhibitors.

TABLE XXIII

Increase in Total Acid Number
Produced by 5 hrs/250°C
Pretreatment
of
Corrosion Test

	△ TAN After 5 hrs./250°C Pretreatment
Batch 1/S1	5.8
Batch 2/S1	6.8
Blend 1/AT	1.77

4.3 Completion of Process 2

Batch 1/S1 and Batch 2/S1 were subjected to the remaining part of Process 2 to produce Batch 1/P2 and Batch 2/P2 respectively.

4.3.1 Comparison of Batch 1/P2 with Batch 1/P1

Test data comparing Batch 1/P2 with Batch 1/P1 are shown in Table XXIV, in which it is seen that Process 2 was effective in bringing about the following changes in the vacuum-steam stripped Batch 1 consignments.

a. Improvement in appearance; the latter was similar in colour to many unused commercial 3 cSt gas turbine lubricants containing no quinizarin.

b. Lowering of 100°F and 210°F viscosities.

c. Improvement in viscosity/temperature slope between 100°F and 210°F from which it was conjectured on the basis of experience that the viscosity of Batch 1/P2 @ minus 65°F was unlikely to exceed 13,000 cSt.

d. Lowering of copper and iron contents below 1 p.p.m.

With regard to additives, it is pertinent to note that no significant loss in phosphorus content, or in chlorine level, occurred during the process.

Also shown in Table XXIV are the concentrations of inhibitors found in each batch. These were determined by HPLC analysis (Appendix IV) excepting quinizarin which was tested for qualitatively by the calcium hydroxide test introduced in 3.5. It is seen that apart from loss of quinizarin, no substantial losses in these inhibitors occurred during the process.

4.3.2 Comparison of Batch 2/P2 with Batch 2/P1

Test data comparing Batch 2/P2 with Batch 2/P1 are presented in Table XXV.

The improvements gained upon application of Process 2 to the vacuum-steam stripped Batch 2 consignments are seen to be similar to those obtained in the case Batch 1/P1 and, as with the latter, no significant change occurred in phosphorus content and chlorine level.

It is also seen here again that apart from loss of quinizarin, the application of Process 2 produced no substantial losses in the determined inhibitor contents of Batch 2/P1.

4.3.3 Effect of Process 2 Upon Corrosivity

Batch 2/S1 was shown under 4.2.1 to be contentious in respect of it's corrosive action on cupro materials.

Tables XXV1A and XXV1B show the metal weight changes and appearances of the test specimens respectively at the end of similar corrosion tests carried out on Batch 1/P2 and Batch 2/P2.

TABLE XXIV

		Batch 1/P1	Batch 1/P2
Yield (as per cent of Batch 1/P1)		100	92
Transparency		Dull	Sparkling Clear
Colour		Dark Reddish Brown	Amber
Flash Point °F (ASTM.D92)		440	425
Specific Gravity 60°F/60°F		0.939	0.937
Kinematic Viscosity cS	@ 210°F	3.39	3.17
	@ 100°F	13.4	12.5
Total Acid Number - mgKOH/g		0.63	0.03
Saponification Value - mgKOH/g		293	293
Phosphorus % (expressed as P)		0.078	0.080
Chlorine Level (Lassaigne's Test)		Traces (Group 1)*	Traces (Group 1)*
Iron Content - p.p.m.		11	0.17
Copper Content - p.p.m.		1.03	0.27

Antioxidants

NADOPT %	0.03	nf.
DODP %	1.33	1.41
MOPAN %	0.09	0.08
PAN %	0.15	0.17
DOPT %	0.01	0.01
PTZ %	nf.	nf.
Quinizarin	Present	Absent

nf. - not found

* See Table IV

TABLE XXV

		Batch 2/P1	Batch 2/P2
Yield (as per cent of Batch 2/P1)		100	92
Transparency		Dull	Sparkling Clear
Colour		Dark Reddish Brown	Pale Amber
Flash Point °F (ASTM. D92)		445	415
Specific Gravity 60°F/60°F		0.946	0.944
Kinematic Viscosity cSt	@ 210°F	3.37	3.16
	@ 100°F	13.3	12.4
Total Acid Number - mgKOH/g		0.40	0.08
Saponification Value - mgKOH/g		303	305
Phosphorus % (expressed as P)		0.082	0.081
Chlorine Level %		0.09*	0.09* 0.08**
Iron Content - ppm		6.7	0.26
Copper Content - ppm		0.45	0.27

Antioxidants

NADOPT %	nf	nf
DODP %	0.94	0.99
MOPAN %	0.31	0.26
PAN %	0.12	0.15
DOPT %	nf	nf
PTZ %	nf	nf
Quinizarin	Present	nf

nf = not found

* IP.118/65 (Joint ASTM D.1317-64) except for titration of sodium chloride with silver nitrate potentiometrically

** Fusion with potassium followed by gravimetric determination of silver chloride

TABLE XXVIA

Corrosivity - 192 hours/150°C. Corrosion (R.R. 1002) After Pretreatment of Sample by 5 hours/250°C. Confined Heating (R.R. 1003/Supp. 1)

TEST SPECIMEN	Metal Weight Change in mg/cm^2					
	Batch 1/P2	Batch 2/P2	TEL.0029	Batch 2/ S1-HS1	Blend 1/AT	Rolls Royce Requirements
Magnesium Alloy	-6.1	-2.5	+2.4	-5.1	-3.3	Report
Aluminium Alloy	<0.1	<0.1	<0.1	<0.1	<0.1	0.1 maximum
Mild Steel	<0.1	<0.1	<0.1	<0.1	<0.1	0.1 maximum
Soldered Copper	<0.1	-3.2	-3.2	<0.1	<0.1	3.0 maximum
Lead	-24	-21	-31	-34	-61	Report
Copper	-0.30	-0.87	-0.34	<0.05	<0.05	1.0 maximum
Brass	-3.0	-3.3	-1.1	<0.1	<0.1	4.0 maximum

Note: Results for Batch 1/S1 and Batch 2/S1 given in Table XXIIA

TABLE XXVIB

Corrosivity - 192 hours/150°C. Corrosion (R.R. 1002) After Pretreatment of Sample by 5 hours/250°C. Confined Heating (R.R. 1004/Supp. 1)

TEST SPECIMEN	Appearance of Specimen					
	Batch 1/P2	Batch 2/P2	TEL.0029	Batch 2/ S1-HS1	Blend 1/AT	Rolls Royce Requirements
Magnesium Alloy	$D_g(x)$* $E_g(x)$	$D_g(x)$ $P_g(x)$	$D_g(x)$ $P_g(x)$	$D_g(x)$ $P_g(x)$	$D_g(x)$ $P_l(m)$	Report
Aluminium Alloy	0	0	0	0	0	No Etching or Pitting
Mild Steel	0	0	0	0	0	No Etching or Pitting
Soldered Copper	$D_g(m)$ $E_g(m)$	$D_g(x)$ $E_g(x)$	$D_g(x)$ $E_g(x)$	$D_g(s)$	$D_g(s)$	Report
Lead	$D_g(x)$*	$D_g(m)$* $E_g(x)$	$D_g(m)$ $E_g(s)$	$D_g(m)$	$D_g(s)$ $E_g(x)$	Report
Copper	$D_g(m)$ $E_l(m)$	$D_l(s)$ $E_g(m)$	$D_g(m)$ $E_l(m)$	$D_g(s)$	$D_g(s)$	Report
Brass	$D_g(m)$	$D_g(m)$ $E_g(m)$	$D_g(m)$ $E_g(x)$	$D_g(s)$	$D_g(s)$	Report

Descriptive Key:- 0 = no change; E = etched; l = local; (s) = slight; (x) = excessive
D = discoloured; P = pitted; g = general; (m) = moderate; * = depositon of Copper

Note:- Results for Batch 1/S1 and Batch 2/S1 given in Table XXIIB

These results are not significantly different from those obtained for Batch 1/S1 and Batch 2/S1, the remaining part of Process 2 therefore having brought about no significant reduction in corrosion of the cupro specimens.

Also shown in Tables XXV1A and XXV1B are the results obtained for the unused lubricant TEL 0029 which is seen to be less corrosive towards copper and brass than Batch 2/P2. This was of interest in that TEL 0029 was found to contain a relatively high chlorine content as shown in Table XXV11 giving the determined chlorine contents of the TEL series of unused lubricants.

The high chlorine content of TEL 0029, and the fact that it exceeded the chlorine contents of Batch 1 and 2 consignments supported the hypothesis that the chlorine in these consignments was derived from an intentional component of one or more of the lubricants present rather than from a contaminant; the relatively high corrosivity of Batch 2/P2 was believed to be most probably due to deficiencies in inhibitors.

The copper and brass weight losses produced in the corrosion tests by the two batches of Processed 2 lubricants, and the unused lubricants tested, are collected together in Table XXVIII in which the lubricants are arranged in descending order of their corrosiveness towards these metals.

ATL 9101 is seen, by these criteria, to be the most, and ATL 9102 the least corrosive of the unused lubricants, with TEL 0029 falling between these two, and the most corrosive lubricant of all being Batch 2/P2.

4.4 Inhibitor System HS1

Since no information was available on the additive contents of the lubricants from which the consignments had been derived, it was decided, on the basis of experience, to bring the inhibitor contents of the processed consignments up to the levels shown in Table XXIX for an inhibitor system designated by Dalton as HS1.

4.4.1 Effect of Inhibition Upon the Corrosivity of Batch 2/S1

In view of the contentious corrosivity of Batch 2/S1 highlighted earlier, the efficacy of the inhibitor system in lowering the corrosiveness of this material in particular, was firstly examined by carrying out a corrosion test on a sample of Batch 2/S1 after having raised it's inhibitor contents to the levels of HS1.

The proportions of inhibitors added, and the determined inhibitor contents, before and after these additions, are presented in Table XXX in which the inhibited material is designated Batch 2/S1-HS1 to distinguish it from Batch 2/S1. The determination of inhibitors, apart from quinizarin, was carried out by HPLC analysis under the conditions in Appendix IV. Quinizarin was determined by visible spectroscopy using the "peak height" technique explained in Appendix IX in which the investigation, that led to this technique, is described.

TABLE XXVII

Chlorine Contents
of
TEL Series
of
Unused Lubricants

Lubricant	Chlorine %
TEL.0026	Approx. 0.003*
TEL.0027	Less than 0.001*
TEL.0028	Less than 0.001*
TEL.0029	0.245 **

* Adjudged from Lassaigne's Test

** IP.118/65 (Joint ASTM D.1317-64) except for titration of sodium chloride with silver nitrate potentiometrically

TABLE XXVIII

Descending Order of Corrosivity
In Terms of
Copper and Brass Weight Losses

Lubricant	Metal Weight Loss - mg/cm^2	
	Copper	Brass
Batch 2/P2	0.87	3.3
Batch 1/P2	0.30	3.0
ATL.9101	0.42	2.1
TEL.0029	0.34	1.1
ATL.9100	Less than 0.05	0.60
ATL.9102	0.06	0.20

TABLE XX1X

INHIBITOR SYSTEM HS1

Inhibitor	% w/w in Final Product
BTZ (Benzotriazole)	0.05
Quinizarin (1,4-dihydroxyanthraquinone)	0.05
PAN (N-phenyl-1-naphthylamine)	0.50
MOPAN (N-4-octylphenyl-1-naphthylamine)	1.00
DODP (4,4'-dioctyldiphenylamine)	1.25

TABLE XXX

Inhibitor Contents of Batch 2/S1-HS1 from Inhibition of Batch 2/S1			
Inhibitors	Batch 2/S1		Found* after Inhibition to produce Batch 2/S1-HS1
	Found* before Inhibition	Inhibitors Added	
NADOPT %	nf	nil	nf
DODP %	0.94	0.31	1.24
MOPAN %	0.3	0.7	0.98
PAN %	0.1	0.4	0.50
DOPT %	nf	nil	nf
PTZ %	nf	nil	nf
BTZ %	0.002	0.05	0.04
Quinizarin %	nf	0.05	0.047
Anthranilamide %	nf	nil	nf

* HPLC Analysis except for Quinizarin

nf = Not found

The results of the corrosion test on Batch 2/S1-HS1 may be seen upon returning to Tables XXVIA and XXVIB.

A dramatic improvement is seen upon comparing the losses in weight of soldered copper, copper and brass in the inhibited material with those shown for Batch 2/S1 in Tables XXIIA and XXIIB.

The discolorations (Table XXIIB) observed with the metal specimens in Batch 2/S1-HS1 took the form of very thin glossy irridescent films exhibiting optical interference colours indicative of effective passivation.

It is also of interest to note from the results that Batch 2/S1-HS1 was less corrosive towards the cupro metals than any of the four unused lubricants tested.

4.5 Blend 1 - Production

The reason for bulking the used lubricant consignments in two separate batches was, as already explained, the relatively high chlorine contents of those from which Batch 2 was produced and, in the absence of positive identification of the chlorine-containing material, some uncertainty as to whether these would be reclaimable by the Dalton technology.

This uncertainty was afterwards largely removed by the satisfactory corrosion results obtained upon inhibition of Batch 2/S1, and from which it was concluded that Batch 2/P2 likewise inhibited would give satisfactory corrosion results, thereby leaving less justification for continuing to divorce the two batches, especially since the quantities available of Batch 1/P2 and Batch 2/P2 were insufficient for production of 1000 gallons of reclaimed lubricant from each.

The only other justification warranting production of the smaller quantity of reclaimed lubricant possible from each batch was if one were substantially richer in polyol ester content than the other. However, the specific gravities and saponification values obtained for Batch 1/P2 and Batch 2/P2 indicated that this was not so, as also did the results of IR spectrum analyses.

It was therefore decided to conduct the remaining part of the reclamation viz. additive treatment, on a blend of Batch 1/P2 with Batch 2/P2, using as much of the latter as possible in the blend in the interest of extending knowledge on the application of the technology to used lubricant containing unremovable chlorine compounds.

The quantities of Batch 1/P2 and Batch 2/P2 available amounted to 430 and 908 US gallons. Accordingly, 1000 gallons of Processed 2 material, designated "Blend 1" were prepared by blending 90 per cent by weight of Batch 2/P2 with 10 per cent by weight of Batch 1/P2, the blending plant employed having been cleaned and flushed out by utilising surplus Batch 1/P2 for this purpose.

4.5.1 Additive Treatment Scheme

The additive treatment schemed for Blend 1 was to bring the inhibitor contents of the blend up to the levels of HS1 to produce "Blend 1-HS1", and then to complete the treatment by incorporating in the inhibited blend 0.5 per cent of a load-carrying agent designated by Dalton as "LCA.7" to produce Blend 1/AT, i.e., the finished reclaimed lubricant.

The process status designations employed in this scheme are collected together in Table XXXI.

4.6 Blend 1/AT - Laboratory Preparation

The inhibitor contents of a sample taken from the 1000 gallons of Blend 1 were firstly increased to the levels of HS1 in Table XXIX to produce a sample of Blend 1-HS1. The proportions of inhibitors added, and the determined inhibitor contents, after these additions, are presented in Table XXXII in which also are recapitulated the determined inhibitor contents of the component batches of Blend 1 from which the innibitor contents of the latter also shown, were calculated. 0.5 per cent by weight of additive LCA.7 was then incorporated in the inhibited sample to produce a trial sample of Blend 1/AT.

4.7 Assessment of Laboratory Blend 1/AT

The results of corrosion tests carried out on the above laboratory preparation of the finished product are given in Tables XXVIA and XXVIB , and those of other tests which were carried out are collected together in Table XXXIII. The following comments are relevant:-

4.7.1 Appearance

The change in colour produced upon additive treatment of Process 2 material was due to the colours of the quinizarin and MOPAN additions.

4.7.2 Viscosity

Comparison of the viscosity results in Table XXXIII with those for Batch 1/P2 and Batch 2/P2 in Tables XXIV and XXV respectively shou that the additive treatment had not altered the viscosity of Blend 1 @ 210°F, but had produced a small increase in ASTM viscosity/temperature slope. Measurements below minus 34°F were precluded by the limitations of the low-temperature viscosity bath available, but it was believed, from consideration of the results obtained at the three temperatures in Table XXXIII, and experience with other lubricants, that the viscosity of the material @ minus 65°F would lie in the neighbourhood of 13,000 cSt, i.e., below the specification maximum of 17,000 cSt

TABLE XXXI

Process Status Designations

Blend 1	=	90% Batch 2/P2 + 10% Batch 1/P2
Blend 1-HS1	=	Blend 1 Inhibited to HS1 Inhibitor System Level
Blend 1/AT	=	(Blend 1-HS1) + 0.5% Load-carrying additive LA.7

TABLE XXXII

INHIBITOR CONTENTS - BLEND 1-HS1

	Determined in:-		C	D	Blend 1-HS1	
	A Batch 2/P2	B Batch 1/P2	Calculated from A and B Blend 1*	Added to C	Determined in Blend 1 + D	Calculated from C and D
DODP %	0.99	1.41	1.03	0.22	1.24	1.25
MOPAN %	0.26	0.08	0.24	0.76	1.15	1.0
PAN %	0.15	0.17	0.15	0.35	0.53	0.5
BTZ %	nf	nf	nil	0.05	0.066	0.05
Quinizarin %	nf	nf	nil	0.05	0.05	0.05

* Blend 1 = 90% Batch 2/P2 + 10% Batch 1/P2

nf = Not found

TABLE XXXIII

ASSESSMENT TESTS - LABORATORY TRIAL BLEND 1/AT

Transparency			Sparkling Clear
Colour			Light orange
Flash Point ^{O}F (ASTM.D.92)			440
Kinematic Viscosity - cSt	@ 210^{O}F		3.17
	@ 100^{O}F		12.7
	@ minus 34^{O}F (48 hrs soak)		847
Total Acid Number - mgKOH/g			0.29 (0.05)*
Hydrolytic Stability (RR.1006, Iss. 2)	$D^{90}_{1.5}$ - Hrs		108
	$D^{70}_{1.5}$ - Hrs		725
	$D^{40}_{1.5}$	Hrs	12,608
		Lunar months	19
Foaming Propensity (Method 3213)	Max. Foam - ml		70
	Foam Collapse - secs		21
Coking Propensity - mg Deposit (Appendix IV - Stainless Steel dish)	@ 250^{O}C		<2
	@ 275^{O}C		<2
Iron Content - ppm			0.25
Copper Content - ppm			<0.3

* Results in brackets obtained by titrating to a pH 11 end point using ASTM.D.664

4.7.3 Total Acid Number - Determination

Except where otherwise indicated, total acid numbers in the present report were determined in accordance with a modification of IP.1 Method A (joint IP/ASTM.139/D.974), the modification consisting of titrating the sample in the cold with aqueous standard alkali. The titrations were carried out potentiometrically when the rate of pH change in the neighbourhood of the assumed stoichiometric end point corresponding to pH11 was so slow as to give rise to difficulty in discerning the colour change of the alkali-blue indicator. This is the procedure customarily employed by Dalton as a matter of convenience since aqueous standard alkali requires less frequent standardisation than standard alcoholic potash, and no significant saponification of diester and polyol ester base stocks has been observed with aqueous alkali provided the titration is carried out in the cold.

The procedure specified in MIL-L-7808H is to titrate to pH11 end point using ASTM.D664 which, depending upon the composition of the lubricant, may or may not, produce different results for total acid number than the foregoing method.

4.7.4 Total Acid Number - Results

Based upon the total acid numbers given for Batch 1/P2 and Batch 2/P2 in Tables XXIV and XXV respectively, the total acid number for Blend 1, when determined by titration with aqueous standard alkali, was calculated to be 0.075 mgKOH/g. Referring to Table XXXIII, it is evident that the additive treatment had brought about an increase of 0.29 - 0.075 = 0.22 mgKOH/g.

This was due to the BTZ component, the amphoteric nature of which is well known, and which is titratable by aqueous alkali, but not by alcoholic potash in non-aqueous media. The fact that BTZ was the only additive component responsible for the increase is illustrated in Table XXXIV, in which are shown the results obtained for concentrates of the additives in Blend 1.

The total acid number of 0.05 mgKOH/g obtained for Blend 1/AT by titration with alcoholic potash to pH11 in accordance with the method specified in MIL-L-7808, is seen in Table XXXIII to be well below the specification limit of 0.30 maximum.

4.7.5 Hydrolytic Stability

Hydrolytic stability was determined @ 90 and 70°C in accordance with Rolls Royce Method 1006, a summary of which is given in Appendix VI.

Tests were carried out also on Batch 1/P2 and Batch 2/P2, i.e., the 10% and 90% components respectively of Blend 1, so that some idea of the effect of additive treatment upon hydrolytic stability could be acquired by comparing the results with those obtained for Blend 1/AT.

Considering firstly the results obtained for Batch 1/P2 and Batch 2/P2, the curves obtained upon plotting acidity increase against test duration are shown in Figs. 5 and 6, interpolation giving the durations producing an acidity increase of 1.5 mgKOH/g @ 90 and 70°C as symbolised by $D^{90}_{1.5}$ and $D^{70}_{1.5}$ respectively in Table XXXV which also gives for each material the calculated value of $D^{40}_{1.5}$ representing the duration which would produce the same acidity increase @ 40°C.

TABLE XXXIV

CONTRIBUTION OF ADDITIVES TO TOTAL ACID NUMBERS OF ADDITIVE/BLEND 1 CONCENTRATES

Blend 1 plus :-	△ TAN
4.4% by weight DODP	<0.1
16.7% by weight MOPAN	<0.1
7.66% by weight PAN	<0.1
1.1% by weight BTZ	4.9 (<0.01)*
0.25% by weight Quinizarin	<0.1
11.0% by weight LCA.7	<0.1

* Result in brackets obtained by titrating to a pH 11 end point using ASTM.D.664

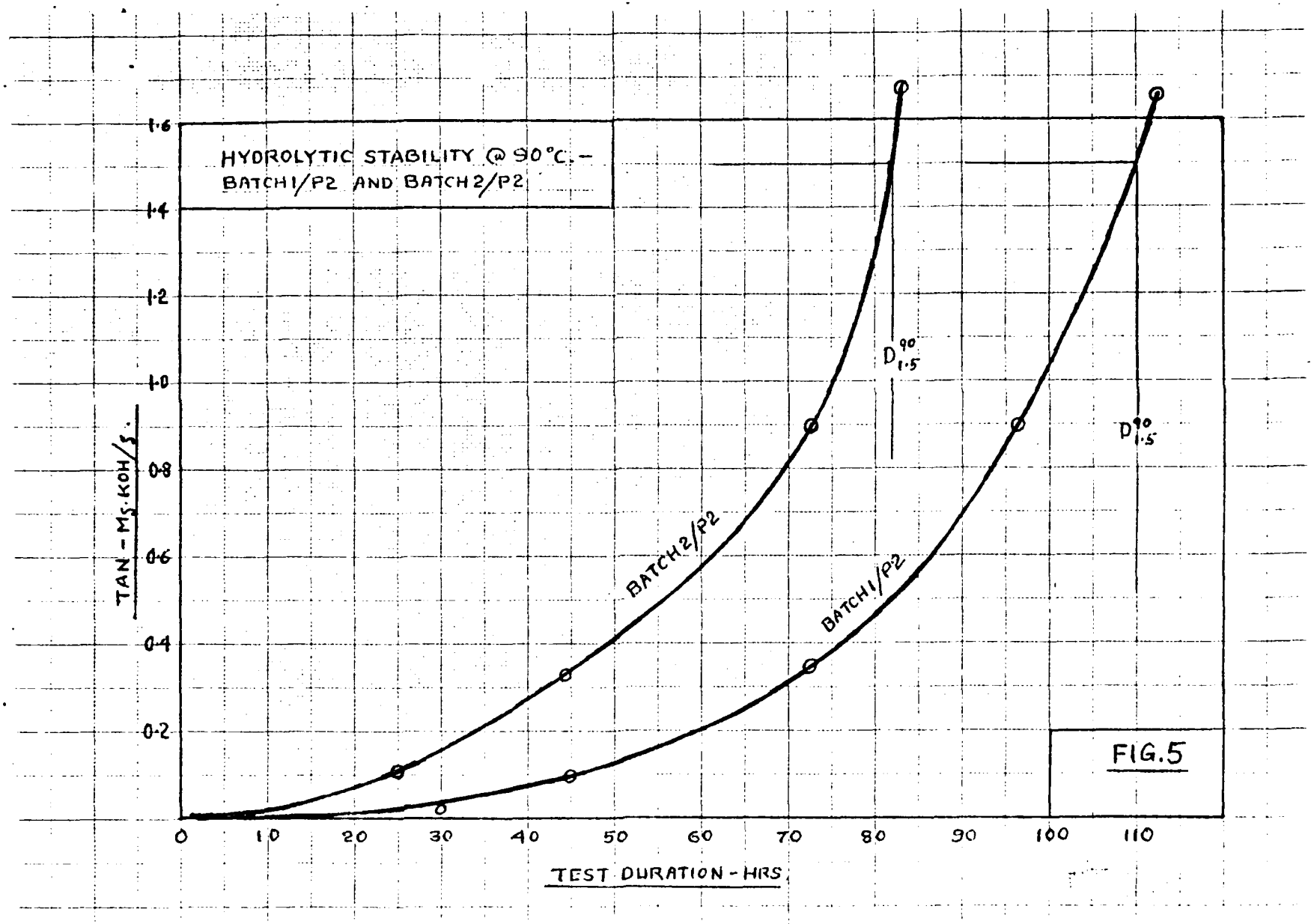

HYDROLYTIC STABILITY @ 90°C. –
BATCH 1/P2 AND BATCH 2/P2
TAN – MS. KOH/S.
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
10
20
30
40
50
60
70
80
90
100
110
TEST DURATION – HRS
BATCH 2/P2
BATCH 1/P2
$D^{90}_{1.5}$
$D^{90}_{1.5}$

FIG.5

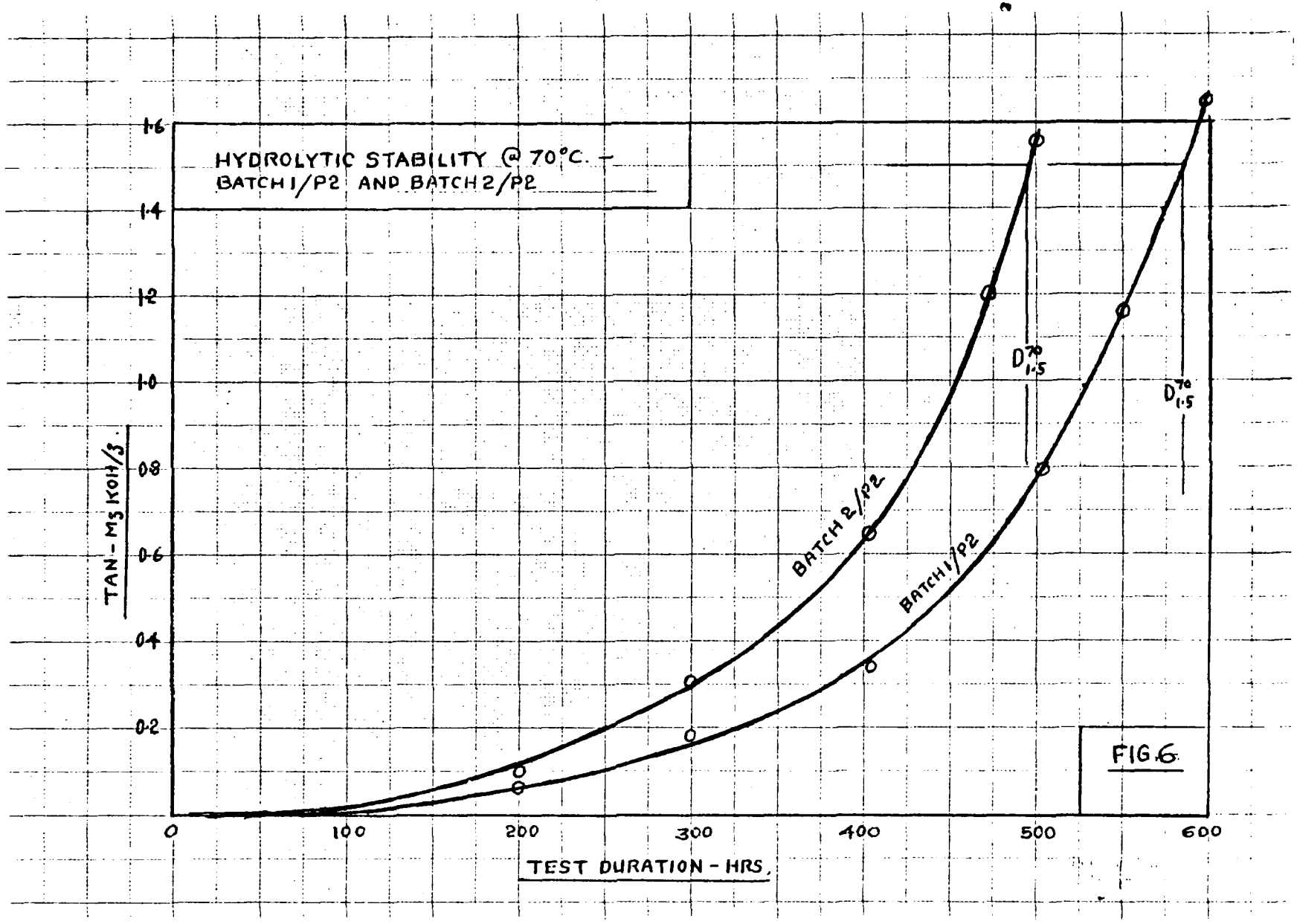

HYDROLYTIC STABILITY @ 70°C. –
BATCH 1/P2 AND BATCH 2/P2
TAN - MG KOH/G.
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
0
100
200
300
400
500
600
TEST DURATION - HRS.
BATCH 2/P2
BATCH 1/P2
$D^{70}_{1\cdot5}$
$D^{70}_{1\cdot5}$

FIG 6

09

TABLE XXXV

Hydrolytic Stability (RR1006, Issue 2)
of
Batch 1/P2 and Batch 2/P2

		Batch 1/P2	Batch 2/P2
$D^{90}_{1.5}$ - hours		110	84
$D^{70}_{1.5}$ - hours		586	493
$D^{40}_{1.5}$	hours	7205*	7010*
	Lunar months	11	10

* Calculated from:-

$$\log D^{40}_{1.5} = 2.5 \log D^{70}_{1.5} - 1.5 \log D^{90}_{1.5}$$

as derived from:-

$$\log D^{\theta}_{1.5} = a - b\theta$$

This hydrolytic stability test is employed by Rolls Royce for the purpose of ensuring that a lubricant candidate will not undergo unacceptably high rates of hydrolysis during storage, minimum permissible shelf-life being specified in terms of $D^{40}_{1.5}$ since a tropical temperature of 40°C is considered to be the most unfavourable temperature likely to be experienced during the storage of lubricant.

$D^{40}_{1.5}$ is calculated from:-

$$\log D^{40}_{1.5} = 2.5 \log D^{70}_{1.5} - 1.5 \log D^{90}_{1.5} \qquad \text{eq. 1,}$$

a relationship which has been derived from tests carried out by Rolls Royce with a large number of synthetic gas turbine lubricants embracing traditional 3.0 cSt, 5.0 cSt, and 7.5 cSt viscosity types.

The requirement in terms of $D^{40}_{1.5}$ depends upon application, examples of which are:-

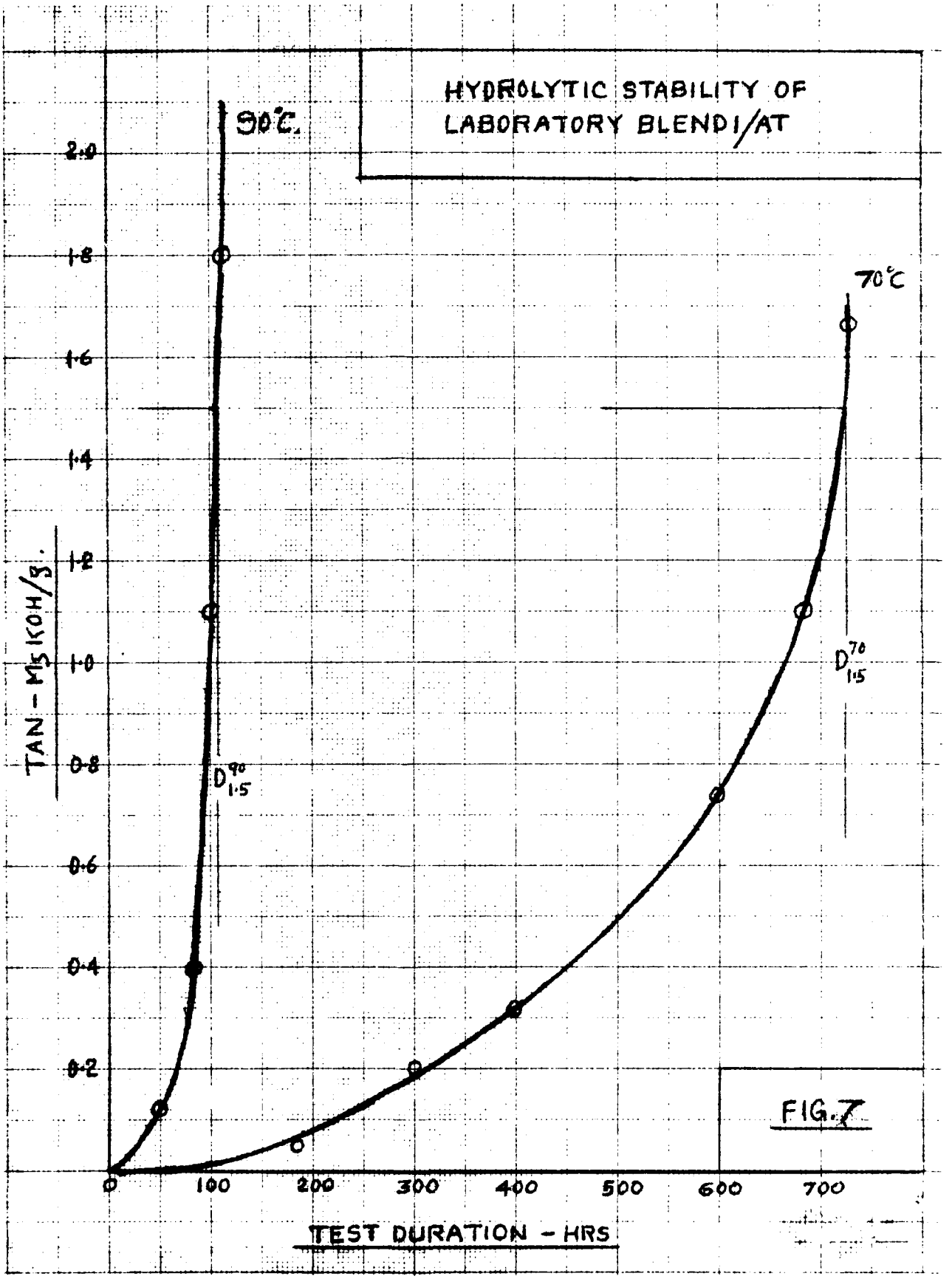
Rolls Royce commercial aircraft gas turbines	650 hrs. min.
Rolls Royce industrial gas turbine systems featuring a large lubricant 'make-up' tank exposed to tropical climates	2000 hrs. min.
Ministry of Defence D.Eng.R.D. 2497	1000 hrs. min.(tentative)

Referring to Table XXXV, it is seen that the hydrolytic stabilities of Batch 1/P2 and Batch 2/P2 were well in excess of these minimum requirements.

Acidity observations by Rolls Royce during lubricant storage periods extending up to ten years have led to an empirical factor of 5 which, multiplied by the hydrolytic stability of the lubricant determined as in the foregoing, gives an approximate indication of the shelf-life of the lubricant when packed in the traditional 45 gallon UK steel barrel. The shelf-lives of Batch 1/P2 and Batch 2/P2 in such circumstances should therefore be of the order of four years at an ambient temperature of 40°C, the acidity increase expected at the end of this period being, by definition, about 1.5 mgKOH/g.

Considering now the results obtained for the hydrolytic stability of Blend 1/AT in Table [illegible] III, it is seen upon comparing these with those obtained for Batch 1/P2 and Batch 2/P2 in Table XXXV that whereas the additive treatment had neither impaired nor improved the stability @ 90°C, it produced a large increase @ 70°C, as may also be seen upon comparing Fig. 7 with Figs. 5 and 6.

The conclusion from these results is that Blend 1/AT possesses exceptional storage stability when assessed in terms of hydrolytic stability in accordance with the procedure explained above. For example, the calculated result for 40°C was 12,608 hours which is interpreted as 5 x 12,608/672 = 94 lunar months or at least 7 years for the storage life of the lubricant in the traditional UK 45 gallon barrel @ 40°C ambient tropical temperature.


HYDROLYTIC STABILITY OF
LABORATORY BLEND I/AT
90°C.
70°C
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
TAN - MG KOH/G.
$D^{90}_{1\cdot5}$
$D^{70}_{1\cdot5}$
0
100
200
300
400
500
600
700
TEST DURATION - HRS
FIG. 7

4.7.6 Corrosivity

Referring to Tables XXVIA and XXVIB, it is seen that Blend 1/AT was no more corrosive towards the cupro metals than Blend 1-HS1, thereby illustrating that the presence of the load-carrying agent had not impaired the reduction in corrosivity brought about by inhibition of Blend 1.

The additive treatment was expected, from experience gained by Dalton in the reclamation of lubricant arisings from commercial aviation and industrial gas turbines, to bring about a substantial improvement in the oxidative stability of Blend 1, and Blend 1/AT was expected to compare favourably in this regard with unused lubricant. Oxidation tests had not been carried out at this stage of the research, but the effectiveness of the treatment in reducing degradation from the combined action of oxidative and thermal stress in the 5 hrs/250°C confined-heat pre-treatment of the corrosion test sample was reflected by an acidity increase of 1.77 mgKOH/g at the end of the pre-treatment compared with increases of 5.8 and 6.8 mgKOH/g for Batch 1/S1 and Batch 2/S1 respectively (Table XXIII).

Comparing Blend 1/AT with Blend 1-HS1 in Table XXVIA, the former is seen to produce a greater loss in the weight of the lead specimen. However, as mentioned earlier, the behaviour of lead under the test conditions employed is so capricious that little significance can be attached to the results, and certainly, they afford no indication of the behaviour of the metal under the conditions of the SOD lead corrosion test specified in MIL-L-7808H.

4.7.7 Lead Corrosion @ 325°F (162.8°C)

Whereas hydrolytic stability @ 40°C is the parameter adopted by Rolls Royce Limited and Dalton in assessing the storage stabilities of gas turbine lubricants, the SOD lead corrosion test specified in MIL-L-7808H is of considerable importance to the AFAPL as an indirect means of assessing stability in their accelerated and extended storage stability test procedures.

In the absence of the equipment specified (Fed. Std. 791-Method 5321) for carrying out the SOD lead corrosion test, an attempt was made to obtain some idea of the influence of the additive treatment upon SOD lead corrosion by carrying out tests under similar environmental conditions, but with a different configuration of test specimens which was the best compromise that could be made under the circumstances. The test conditions were:-

Sample Volume	500 ml
Air Supply	0.940 litres/min
Temperature	325°F ± 2°F
Test Duration	60 mins ± 1 min

The stainless steel rod assembly of metal discs specified in Rolls Royce Method 1002 was adopted, but only the lead and copper discs were employed, four each of which were spaced alternately on the steel rod which was mounted vertically in the lubricant, and rotated @ 600 ± 50 rpm by means of a stirrer motor.

Each disc specimen was thus rotated in a horizontal plane about its centre, whereas in the SOD test, a rectangular lead and copper panel, situated in vertical planes, are rotated about the vertical axis of the stirrer rod to which they are attached. The two methods would not be expected to give the same lead weight changes but it was felt that these would rate lubricants in the same order.

Results obtained by the former procedure for Batch 1/P2, Batch 2/P2, Blend 1 and Blend 1/AT are presented in Table XXXVI. It is seen that Batch 2/P2 produced about twice the lead weight loss as Batch 1/P2, and Blend 1 produced an intermediate result. Additive treatment of Blend 1 however reduced the lead corrosion below the level obtained for Batch 1/P2 as shown by the result for Blend 1/AT.

An SOD lead corrosion test carried out by AFAPL on Batch 1/P2 produced a lead weight loss of 7 mg/in^2 (4), and it would seem reasonable to infer from Table XXXVI that the SOD lead corrosion for Blend 1/AT would be of similar order of magnitude.

It would be of interest to know whether a correlation exists between hydrolytic stability, as defined in terms of the time producing an acidity increase of 1.5 mgKOH/g, and the SOD lead corrosion test duration producing a given lead weight loss, or alternatively, between hydrolytic acidity increase and lead weight loss vs. test duration. The question of test temperature is important, for it is evident upon comparing the hydrolytic stability results for Blend 1/AT (Table XXXIII) with those for Batch 1/P2 (Table XXXV) which are seen to change at different rates with respect to temperature, that if a correlation exist , lead weight losses at different temperatures may rate some lubricants in different order of merit.

4.7.8 Foaming Propensity

The static foaming characteristics observed with Blend 1/AT are seen in Table XXXIII to comply with MIL-L-7808H. Detailed results are presented in Table XXXVII, in which it is seen that the maximum foam volume was attained within the first three minutes of the test, the foam thereafter settling down to 50 to 60 ml.

A second test was run in which however the air supply was turned off immediately the maximum foam volume of 70 ml had been attained. The foam collapsed almost immediately, well within one second.

4.7.9 Coking Propensity

The coking propensity data in Table XXXIII were obtained in accordance with a laboratory static coking test developed by Rolls Royce Limited, a summary of which is given in Appendix VII. The test is considered by Rolls Royce Limited to be meaningful in providing provisional information, on a relative basis, on the potential coking propensities of lubricants in gas turbine operation.

TABLE XXXVI

LEAD CORROSION @ 325°F

	Lead Weight Loss - mg/in^2
Batch 1/P2*	4.3 4.3
Batch 2/P2	8.5 8.5
Blend 1	7.0
Blend 1/AT	3.2

* 7.0 mg/in^2 SOD lead corrosion obtained by AFAPL for Batch 1/P2 when tested in accordance with Fed. Std. 791, Method 5321.

TABLE XXXVII

FOAMING PROPENSITY*
LABORATORY TRIAL BLEND 1/AT

Test Duration - mins	Foam Vol. - ml	Foam Collapse - secs
<3	70	-
5	55	-
10	60	-
15	50	-
20	50	-
25	50	-
30	55	21

* Tested in accordance with Fed. Test Method Standard No. 791B - Method 3213 (AFAPL-1975)

The deposits of less than 2 mg shown for Blend 1/AT are extremely low in comparison with 32 and 25 mg coke which have been obtained at these test temperatures respectively for typical 3.0 cSt diester lubricants. The low results obtained for Blend 1/AT would be expected to be manifested in gas turbine operation by relatively clean 'hot-end' bearing compartments, and less coke from reclassification of oil mist on the walls of other high-temperature localities.

4.7.10 Additive Costs Saving

One objective of the reclamation technology is to ensure minimal loss in the additive contents of used lubricant during the processing. This is not only desirable on economy grounds, but also in regard to the conservation of additives, and problems in the disposal of waste chemicals.

The prices in the UK of the inhibitors employed in Blend 1/AT were:-

DODP	£3.62 per Kg
MOPAN	£6.22 per Kg
PAN	£18.1 per Kg
BTZ	£12.5 per Kg
Quinizarin	£21.0 per Kg

Based upon these prices, and the data in columns C and D of Table XXXII, the costs of the inhibitors retained in Blend 1, and the costs of those added in producing Blend 1/AT, work out as in Table XXXVIII.

Thus, inhibitors retained during the reclamation are tantamount to a cost saving of £283.6 per 1000 US gallons lubricant, this representing 283.6 x 100/(283.6 + 484.4) = 37% of the cost of the inhibitor contents of Batch 1/AT.

An exact estimate of the saving in total additive costs cannot be made since the load-carrying agents in Blend 1 were not identified. However, it is reasonable to infer, from the phosphorus and chlorine contents of Batch 1/P1 and Batch 1/P2 in Table XXIV and Batch 2/P1 and Batch 2/P2 in Table XXV, that no losses in the load-carrying agent contents of the vacuum-steam stripped consignments had occurred during Process 2, and it is most unlikely that losses in these materials would have occurred during vacuum-steam stripping (Process 1).

Based upon these considerations, the amount of LCA.7 introduced during the additive treatment of Blend 1 was limited to 0.5% on the assumption that the load-carrying agents retained in the blend would be at least equivalent in performance to 2% tritolyl phosphate, the cost of which, at the UK price of £1.20 per Kg, works out at £85.4 per 1000 US gallons lubricant. This would bring the saving in total additive costs to £283.6 + £85.4 = £369.0 per 1000 US gallons lubricant, and which represents 41% of the cost of the total additives content of the reclaimed lubricant, the UK price of LCA.7 being £3.02 per Kg.

TABLE XXXVIII

	Cost (£ per 1000 U.S. gallon Lubricant) of:-	
	Inhibitors Retained	Inhibitors Added
DODP	132.7	28.3
MOPAN	53.1	168.2
PAN	97.8	228.3
BTZ	-	22.2
Quinizarin	-	37.4
TOTAL	283.6	484.4

4.8 Blend 1/AT – Production

Following the apparently satisfactory results obtained upon additive treatment in the laboratory of the sample taken from Blend 1, the whole of the blend was converted to Blend 1/AT by introducing the appropriate additives, i.e. inhibitors in accordance with column D of Table XXXII, and 0.5% by weight of the load-carrying agent LCA.7.

The treated material was than run into lined steel barrels as normally employed by Dalton for reclaimed gas turbine lubricant. These barrels have a high standard of cleanliness, but in view of the stringent requirements of MIL-L-7808H in respect of foaming propensity, which was thought might be sensitive to trace contamination, the additional precaution was taken of utilising about 100 gallons of the reclaimed lubricant for flushing out the barrels (approximately 5 gallons per barrel) before filling them with the lubricant.

4.8.1 The results of tests, other than oxidation, carried out on a representative sample of this production of finished reclaimed lubricant are presented in Tables XXXIX, XXXXA and XXXXB. These are seen to differ but little from those of corresponding tests, in Tables XXXIII, XXVIA and XXVIB respectively for the laboratory trial Blend 1/AT.

4.8.2 Oxidative Stability

The oxidative stability of the material was finally assessed in accordance with the test procedure specified in Rolls Royce method 1001/Supp. 1 and 2, a summary of which is given in Appendix VIII. Sufficient tests were run to obtain, for each of the degradation modes comprising volatilisation loss, acidity increase, viscosity increase and benzene insolubles increase, the effective life of the lubricant, as defined in (5), @ 180°C and 225°C.

The results are presented in Tables XXXXI and XXXXII in which also are given for comparison the results obtained at these temperatures for the unused lubricants ATL9100, ATL9101 and ATL9102. It is seen that the production Blend 1/AT compared favourably in oxidative stability with one or more of these unused lubricants.

The effective-lives of these lubricants at other temperatures may be obtained from the above values @ 180 and 225°C and the following expression which is derived from an inverse form of the Arrhenius relationship connecting reaction rate with temperature:-

$$\log D = 0.2186 \times \frac{E_a}{\theta^o} - \log m$$

in which D is the effective-life in hours of the lubricant @ temperature θ^o in degrees Kelvin, E_a is the apparent activation energy in calories degree^{-1} mole^{-1} of the oxidation process and, for a given lubricant and degradation mode, m is a constant embodying the effective collision number and active masses of the reacting species.

TABLE XXXIX

ASSESSMENT TESTS - PRODUCTION BLEND 1/AT

Transparency			Sparkling Clear
Colour			Light Orange
Flash point ^{o}F (ASTM D.92)			435
Kinematic Viscosity - cSt	@ 210^{o}F		3.18
	@ 100^{o}F		12.8
	@ minus 34^{o}F (48 hrs soak)		850
Total Acid Number - mgKOH/g (Note 1)			0.05
Saponification Value			300
Phosphorus (as P%) (Note 2)			0.11
Chlorine Level % (Note 3)			0.09
Hydrolytic Stability (RR.1006, Issue 2)	$D^{90}_{1.5}$ - hrs		112
	$D^{70}_{1.5}$ - hrs		736
	$D^{40}_{1.5}$	hrs	12360
		lunar months	18
Foaming Propensity (Method 3213)	Max. Foam - ml		70
	Foam Collapse - secs		18
Coking Propensity - mg Deposit (Stainless steel dish) (Note 4)	@ 250^{o}C		Less than 2
	@ 275^{o}C		Less than 2
Iron Content - ppm			0.20
Copper Content - ppm			Less than 0.1

Note 1: Titrated to pH11 end point using ASTM D.664

Note 2: Determined in accordance with ASTM D1091

Note 3: Determined in accordance with IP.118/65 (Joint ASTM D.1317-64) except for titration of sodium chloride with silver nitrate potentiometrically.

Note 4: Determined in accordance with summary under Appendix IV of Progress Report No. 7.

TABLE XXXXA

Corrosivity - 192 hours/150°C. Corrosion (R.R. 1002) After Pretreatment of Sample by 5 hours/250°C. Confined Heating (R.R. 1004/ Supp. 1)

TEST SPECIMEN	Metal Weight Change in mg/cm^2					
	Blend 1/AT Prod. Batch					
Magnesium Alloy	-1.4					
Aluminium Alloy	<0.1					
Mild Steel	<0.1					
Soldered Copper	<0.1					
Lead	-45					
Copper	<0.05					
Brass	<0.1					

TABLE XXXXB

Corrosivity - 192 hours/150°C. Corrosion (R.R. 1002) After Pretreatment of Sample by 5 hours/250°C. Confined Heating (R.R. 1004/Supp. 1)

TEST SPECIMEN	Appearance of Specimen					
	Blend 1/AT Production Batch					
Magnesium Alloy	Eg (m) Dg (m)					
Aluminium Alloy	D					
Mild Steel	D					
Soldered Copper	Dg (s)					
Lead	Eg (m)					
Copper	Dl (s)					
Brass	Dg (s)					

Descriptive Key:-

D = no change; D = discoloured; E = etched; P = pitted; l = local; g = general; (s) = slight; (m) = moderate; (x) = excessive; • = depositon of Copper

TABLE XXXXI

Effective Life in Hours @ 180°C

Degradation Mode	ATL9100 (Polyol Ester)	ATL 9101 (Diester)	ATL9102 (Polyol/Diester Blend)	Production Blend 1/AT
Volatilisation Loss	76	66	155	60
Acidity Increase	>1000	100	100	>1000
Viscosity Increase	200	190	780	200
Benzene Insolubles Increase	620	>1000	750	>1000

TABLE XXXXII

Effective Life in Hours @ 225°C

Degradation Mode	ATL9100 (Polyol Ester)	ATL9101 (Diester)	ATL9102 (Polyol/Diester Blend)	Production Blend 1/AT
Volatilisation Loss	13	15	8½	16
Acidity Increase	9½	3½	11	9½
Viscosity Increase	11	88	3½	25
Benzene Insolubles Increase	110	130	105	103

The lubricant parameters determining effective-life are thus E_a and m, E_a governing the rate at which the effective life changes with temperature. A straight line of constant degradation level is obtained in accordance with the above equation, upon plotting on log-linear paper co-ordinates, D against reciprocal temperature. Such plots, for the above lubricants, may be readily constructed on log-linear paper by drawing straight lines through the determined pairs of effective-life ordinates @ 1/(180 + 273) and 1/(225 + 273) reciprocal temperature degrees Kelvin.

It may be of interest to mention that the oxidative stabilities of the 3 cSt polyol ester lubricants have been observed to decrease much more rapidly with rising temperature, as manifested by steep inverse Arrhenius plots due to large values of E_a, than has been observed with typical 3 cSt diester and 5 cSt polyol ester lubricants employed in commercial gas turbine operation. Very accurate temperature control is therefore necessary in determining the effective-lives of the 3 cSt polyol ester lubricants.

5. UNUSED LUBRICANTS

Results of tests carried out on the three ATL and four TEL unused lubricants are collected together in Tables XXXXIII and XXXXIV respectively.

Referring to Table XXXXIII, it is seen that whereas DODP and PAN were the only antioxidants found in ATL.9100 and ATL.9102, the diester lubricant ATL.9101 was found to contain not only these, but DODP and PTZ as well. The presence of significant concentrations of DODP and PTZ together is somewhat surprising, since the alkylated derivative of PTZ was originally developed to overcome "phenothiazine dirtiness" (6) which arose from the limited solubility in diester base-stocks of PTZ oxidation products.

The low phosphorus content of ATL.9101 is also unusual for a 3 cSt diester lubricant which typically, would be expected to have a phosphorus content of the order of 0.09% in the form of 1.0% tritolyl phosphate.

The high DODP content of ATL.9101 is of further interest, the whole antioxidant package in fact suggesting an attempt to stretch the oxidative stability of this diester lubricant from the requirements of MIL-L-7808G to MIL-L-7808H. Comparison of the oxidative stability of this diester lubricant with that of the polyol ester lubricant ATL.9100 is therefore of some interest. Thus, returning to the effective-life data in Tables XXXXI and XXXXII, it is seen that:-

(a) The relative merits of any two lubricants in respect of oxidative stability depends upon temperature and the particular mode of degradation under consideration.

(b) In terms of effective-life as limited by acidity increase, the oxidative stability of ATL.9101 is less than that of ATL.9100 @ both 180 and 225°C.

(c) In terms of effective-life as limited by viscosity increase, the oxidative stability of ATL.9101 is comparable with that of ATL.9100 @ 180°C, but is greater than that of ATL.9100 @ 225°C.

TABLE XXXXIII

		ATL.9100	ATL.9101	ATL.9102
Kinematic Viscosity cSt	@ 210°F	3.42	3.60	3.44
	@ 100°F	14.6	13.6	13.9
Specific Gravity 60°F/60°F		0.965	0.930	0.941
Saponification Value - mgKOH/g		388	277	286
Total Acid Number - mgKOH/g*		0.07	0.48 (0.50)	0.10
Phosphorus % (expressed as P)		0.044	0.0044	0.144
Chlorine %		Traces	nf	Traces

ADDITIVES

Peak No. 1 NADOPT %	nf	nf	nf
" " 2 DODP %	1.28	2.31	1.14
" " 3 MCPAN %	nf	nf	nf
" " 4 PAN %	1.25	0.12	0.56
" " 5 DOPT %	nf	0.26	nf
" " 6 PTZ %	nf	0.28	nf
" " 7 N-Benzyl 3,7-DOPT	nd	nd	nd
BTZ %	nf	nf	nf
Anthranilamide %	nf	nf	nf
Quinizarin %	nf	Present	nf

nf = not found

nd = not determined

* Results in brackets obtained by titrating to a pH 11 end point using ASTM. D.664

TABLE XXXXIV

		TEL.0026	TEL.0027	TEL.0028	TEL.0029
Kinematic Viscosity cSt	@ 210°F	3.50	3.20	3.29	3.56
	@ 100°F	12.9	12.9	13.5	14.4
Specific Gravity 60°F/60°F		0.928	0.956	0.951	0.952
Saponification Value - mgKOH/g		281	319	315	324
Total Acid Number - mgKOH/g*		0.22 (0.24)	0.47 (0.41)	0.35 (0.16)	0.27 (0.20)
Phosphorus % (expressed as P)		nd	nd	nd	0.20
Chlorine %		Trace **	S. trace ***	S. Trace ***	0.245 ****

Additives (By HPLC)

Peak No. 1	NADOPT %	nf	nf	nf	nf
Peak No. 2	DODP %	1.96	1.24	0.96	0.68
Peak No. 3	MOPAN %	nf	nf	nf	0.69
Peak No. 4	PAN %	nf	1.09	1.02	nf
Peak No. 5	DOPT %	nf	nf	nf	nf
Peak No. 6	PTZ %	nf	nf	nf	nf
Peak No. 7	N-Benzyl 3,7-DOPT	0.5	nf	nf	nf
	BTZ %	nf	nf	0.034	0.012
	Anthranilamide %	nf	nf	nf	nf
	Quinizarin %	0.068	0.019	nf	nf

nd = not determined nf = not found

* Results in brackets obtained by titrating to a pH 11 end point using ASTM.D.664

** Approximately 0.003% as adjudged from Lassaigne's test

*** Less than 0.001% as adjudged from Lassaigne's test

**** IP.118/65 (Joint ASTM D.1317-64) except for titration of sodium chloride with silver nitrate potentiometrically

(d) In terms of effective-life as limited by insolubles increase, the oxidative stability of ATL.9101 is greater than that of ATL.9100 @ both 180 and 225°C.

Incidentally, the above observations reflect the merit in the concept of effective-life as defined in (5) and determined by the procedure of Rolls Royce Method 1001/Supp. 1 and 2. They also highlight the need for caution in drawing conclusions from the more traditional type of oxidation test in which the comparison of lubricants is based upon differences in degradation levels produced under a fixed time/temperature condition.

Referring to Tables XXXXIII and XXXXIV, it is seen that all seven of the unused lubricants conformed to specification in respect of total acid number excepting ATL.9101 and TEL.0029. The high acidities of these may have arisen from hydrolysis during the lapse of time between their production and post examination.

The TEL lubricants were supplied by the AFAPL as representative of more recent lubricants qualified against MIL-L-7808H.

6. CONCLUSIONS/RECOMMENDATIONS

The research carried out has demonstrated the efficiency of the Dalton reclamation technology in recovering about 95% of virgin quality lubricant from USAF used turbine engine lubricant arisings which are reclaimable in the sense of being free of non-removable, harmful contaminants from sources outside the engine environment. The scope of the research was limited, however, to:

a. Used lubricant collected from USAF aircraft at two bases in the UK,

b. collection of the used lubricant in clean barrels supplied by Dalton and

c. adequate supervision of the collection by USAF personnel in accordance with directives implemented by (EOARD, London).

Experience in the reclamation of gas turbine lubricant arisings from commercial aircraft has shown that without exceptionally clean collection equipment and implementation of good housekeeping under close supervision, contamination incurred during the collection of the arisings can reduce the yield of reclaimable lubricant.

Such precautions may not be practicable in the military arena as a result of world-wide operation at a large number of sites and the large number of personnel involved and their frequent changes in position. This leaves open the question of what would be the yield of reclaimable lubricant, on average, from used lubricant collected under prevailing USAF conditions where no special precautions are taken to minimize contamination.

It is recommended that research be carried out with the objective of laboratory screening potentially reclaimable from non-reclaimable samples taken over a protracted period from a representative distribution of USAF bases, followed by a reclamation exercise carried out on a blend of reclaimable samples, and development of a minimum quality specification for used turbine engine lubricant acceptable for reclaiming.

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MIL-L-7808G, 22 Dec., 1967

MIL-L-7808H, 1 Nov., 1977

D.Eng.R.D. 2497, Issue 4 (Draft)

AD-A111 200 DALTON AND CO (SYNTHETIC PRODUCTS) LTD BELPER (ENGLAND) F/G 11/8
RECLAMATION OF SYNTHETIC TURBINE ENGINE LUBRICANTS.(U)
AUG 81 R A MICALLEF, A T SQUIRES F49620-79-C-0073

UNCLASSIFIED AFWAL-TR-81-2072 NL

2 OF 2
AD A111 200

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APPENDIX 1

REPEATABILTIY OF PRELIMINARY INSPECTION

The repeatability of preliminary inspection was investigated by determining the specific gravities, kinematic viscosities @ 210°F and saponification values of samples taken at weekly intervals from the barrels of used lubricant consignments D.587 and D.588.

Total acid numbers, although not suitable for the purpose of the investigation, were also determined to provide provisional information on acidity increase with storage time, a subject which is relevant when considering cases of non-compliance with specification requirements of acid numbers determined on lubricants some time after their dates of preparation. These determinations were not carried out in accordance with ASTM D.664, but by the more convenient modification of IP.1 Method A (Joint IP/ASTM.139/D.974) involving titration of the acidity in the cold with aqueous standard alkali, and which includes any benzotriazole as explained in Section 4.7.4 of the report.

Each sample for testing was taken from a thoroughly shaken blend of three 400 ml aliquots of the consignments, one taken near the top, one half-way down, and the other near the bottom of the up-ended barrel after rolling the latter and up-ending it several times.

The investigation was terminated after eleven samples had been taken from each consignment, over a period of eleven weeks, as there was little to be gained by taking further samples. The results are presented in Table I, and statistics calculated from these results are given in Table II.

Expressing the standard deviations, based on eleven data points, as percentages of the mean, we have:-

Viscosity Limits %		Specific Gravity Limits %		Saponification Value Limits %		Acidity Limits %	
D.587	D.588	D.587	D.588	D.587	D.588	D.587	D.588
0.46	0.24	0.05	Nil	0.32	0.35	3.67	1.56

Comparing D.587 and D.588 in respect of variability, the following conclusions are drawn from consideration of the variance ratios in Table II, and the critical variance ratios for different significance levels as obtained from the F- distribution * for 10,10 degrees of freedom:-

a. D.587 is more variable than D.588 in respect of viscosity (97.5% probability).

b. D.587 is more variable than D.588 in respect of acidity (over 99.9% probability).

* Table V of 'Statistical Tables for Biological, Agricultural and Medical Research (A. Fisher and F. Yates : Oliver and Boyd)

c. The probability of D.588 being more variable than D.587 in respect of saponification value is less than 80%.

d. The variances of the specific gravity results for the two consignments are so small that differences in their variabilities may be ignored.

The statistics calculated from the acidity results, and hence conclusion b. above, may not be valid owing to the disturbing influence of the known tendency of acidity to increase with time. Some indication of this is apparent in the observations made, particularly in the case of D.587, and the variance of acidity among samples taken and tested at the same time would therefore be expected to be less than in the case of samples taken at different times.

The query that led to the present investigation was the validity of having passed D.477 through preliminary inspection when the observed viscosity @ 210°F was only 0.01 cSt above the MIL-L-7808 requirement of 3 cSt minimum. Conclusion a. above, however indicates differences in the variability of viscosity results for different consignments, and the query cannot therefore be resolved specifically without knowledge of the viscosity variance for D.477. This was not investigated as the consignment had been pooled with others in forming Batch 1 feedstock, and at any rate it would be too costly in practice to establish the viscosity variance for every consignment of used lubricant.

Assuming that viscosity results obtained for different samples of D.477 were normally distributed about a mean of say 3.01 cSt with the same variance as D.587, 49% of the results on average would be expected to be not less than 3 cSt, the probability becoming 79% if the variance were the same as for D.588.

The purpose of preliminary inspection is to minimise the risk of including among consignments screened for reclamation any which might jeopardise the reclaimability of the blend. An incorrect decision in passing a marginal viscosity measurement might result in loss of reclaimable material, but it could not lead to the release of unacceptable lubricant for the ultimate criterion is conformance of the reclaimed product with the relevant specification. Furthermore, viscosity is not the only factor taken into account during the inspection of used lubricant. The D.477 gas chromatogram for example indicated that the viscosity of the consignment was more likely to rise than fall during vacuum-steam stripping.

TABLE I

Repeatability of Preliminary Inspection

Date Sampled	Kinematic Viscosity @ 210°F in cSt		Specific Gravity 60°F/60°F		Saponification Value /mgKOH/g		Total Acid Number /mgKOH/g	
	D.587	D.588	D.587	D.588	D.587	D.588	D.587	D.588
79 Dec. 05	3.28	3.37	0.934	0.938	285	295	0.89	0.56
79 Dec. 12	3.28	3.36	0.934	0.938	285	296	0.95	0.57
79 Dec. 19	3.23	3.36	0.933	0.938	287	297	0.96	0.57
80 Jan. 02	3.27	3.37	0.934	0.938	286	297	0.98	0.58
80 Jan. 07	3.28	3.37	0.934	0.938	284	295	1.00	0.58
80 Jan. 14	3.26	3.36	0.934	0.938	285	296	1.00	0.58
80 Jan. 21	3.27	3.38	0.934	0.938	286	297	1.01	0.58
80 Jan. 28	3.26	3.37	0.934	0.938	287	298	0.99	0.57
80 Feb. 06	3.26	3.38	0.933	0.938	286	297	1.00	0.58
80 Feb. 13	3.27	3.37	0.933	0.938	285	297	1.00	0.59
80 Feb. 20	3.28	3.36	0.934	0.938	286	296	1.01	0.59

TABLE II

Preliminary Inspection Statistics

	Kinematic Viscosity @ 210°F. - cS.		Specific Gravity 60°F./60°F.		Saponification Value - mgKOH/g.		Total Acid Number - mgKOH/g.	
	D.587	D.588	D.587	D.588	D.587	D.588	D.587	D.588
Mean	3.267	3.368	0.934	0.938	285.6	296.6	0.98	0.58
Mean Deviation	0.010	0.005	0.0003	0	0.76	0.83	0.030	0.007
Standard Deviation	0.015	0.008	0.0005	0	0.92	1.03	0.036	0.009
95% Confidence Limit for Mean of 11 results	±0.010	±0.005	±0.0003	0	±0.62	±0.71	0.024	0.006
Variance	0.0002	0.00005	1.98×10^{-7}	0	0.846	1.061	0.0013	0.0001
Ratio of Larger to Smaller Variance	4.0		-		1.25		13	

APPENDIX II

GAS-LIQUID CHROMATOGRAPHY

Experimental

The chromatograms of consignments D.471 and D.473 were obtained directly by injecting a sample of each lubricant into the GC equipment which comprised a Tracor 560 operated under the following conditions:-

Column:	5% Dexsil on Chromosorb AW 60/80 mesh 2 m length x 3.2 mm OD.
Carrier Gas:	N_2 @ 50 psi, 20 ml/min
Hydrogen:	40 psi, 30 ml/min
Air:	50 psi, 400 ml/min
Detectors:	Dual FID
Attenuation:	64
Initial Oven Temperature:	200°C
Final Oven Temperature:	350°C
Programme Rate:	5°C/min
Initial Hold:	5 min
Final Hold:	10 min
Inlet Temperature:	350°C
Detector Temperature:	375°C
Sample Size:	0.5 µl

APPENDIX III

INFRA-RED SPECTROSCOPY

Experimental

The infra-red spectra of the unused lubricants and the consignments of used lubricant were obtained by means of a Perkin-Elmer 177 instrument in which the samples were introduced as thin films between sodium chloride plates. Film thickness was not critical, but a very thin film was necessary to accommodate the peaks on the chart. The thickness of the film was so adjusted that the minima of the peaks occurred between 10 to 20% trasmittance in order to ensure consistent results. Scan time was five minutes.

The value of Io for both CH_2 and CH_3 was taken to be the value of the best straight line of the spectrum between 3100 - 3200 cm.

Discussion

It is well known that if an homologous series is studied, it is found that the absorbance of the $-CH_3$ antisymmetric stretch band @ 2960 cm^{-1} is greater than that of the $-CH_2-$ antisymmetric stretch band @ 2930 cm^{-1} where the number of $-CH_2-$ groups is four or less (Fig. 1)

However, as the number of $-CH_2-$ groups along the series is increased, the absorbance of the $-CH_2-$ (anti) stretch band increases until it is greater than that of the $-CH_3$ (anti) stretch band (Fig. 2).

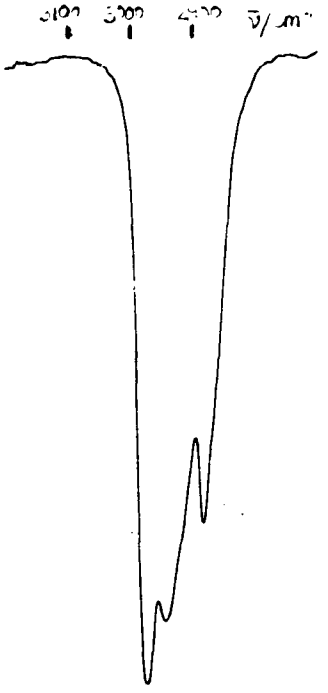


Fig 1

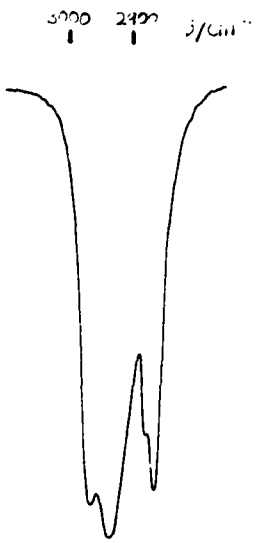


Fig 2

A number of esters were obtained, and it was found that the dibasic acid esters gave an ir pattern as in Fig. 1, whereas the polyol esters gave a pattern as in Fig. 2.

The ratio of $-CH_2-$ groups to $-CH_3$ groups in the molecule was calculated and it was found that the CH_2/CH_3 ratios of 4.5 and less correspond to the pattern as in Fig. 1, and a CH_2/CH_3 ratio of 4.75 and above correspond to the pattern as in Fig. 2.

The structures, together with CH_2/CH_3 ratios are given in Table 1.

Furthermore, it was found that the absorbances of the $-CH_3$ (anti) stretch band and the $-CH_2-$ (anti) stretch band were different in each case.

The absorbance of each band was calculated using the following expression based on Beer's Law:-

$$A \quad \log_{10} \frac{I_o}{I}$$

where A = absorbance
I_o = intensity of incident beam
I = intensity of transmitted beam

The ratio of the absorbances of the $-CH_2-$ and CH_3 bands (i.e. A_{CH_2}/A_{CH_3}) was calculated, and this was plotted against CH_2/CH_3 ratio for each ester type. (Fig. 3).

The ratio of absorbances was calculated because a thin film cell was being used, and so this eliminated the need to know the film thickness.

Although a limited number of esters were studied, it can clearly be seen that each ester type (i.e. 2-ethylhexyl diesters, 2,2,4-trimethylpentyl diesters, trimethylol esters and pentaerythritol esters) forms its own line on the graph.

This is due to the intramolecular structural differences, the absorbance by a particular group being governed by its environment in the molecule, and especially influenced by the presence of oxygen atoms and carbonyl groups.

It was thought that this might also influence the frequency of absorption but after carefully measuring the frequencies of the various bands, it was found that there was no measurable difference between them.

The 2,2,4-trimethylpentyl diesters contain the $C(CH_3)_2$ group. The C-H deformation vibration of this group appears as a doublet at frequencies of 1395 cm^{-1} and 1368 cm^{-1}, and these bands do not appear in the spectra of the other three ester types.

These facts may possibly be used to determine the nature of the base-stock.

For example, two unlabelled oils were received, although it was known that they were di(2,2,4-trimethylpentyl)adipate and di(2-ethylhexyl)adipate, which have a A_{CH_2}/A_{CH_3} ratio of 0.59 and 0.72 respectively.

Sample A was found to have a A_{CH_2}/A_{CH_3} ratio of 0.71, and Sample B was 0.59, showing that A was di(2-ethylhexyl)adipate, and B was di(2,2,4-trimethylpentyl) adipate.

It was also thought that this technique may be useful in determining the concentrations of polyol ester and diester in a mixture. It was realised from the outset that this would be impossible in a totally unknown oil, but it was thought worthy of investigation in any case.

Since the supplied unused oils comprised a diester (ATL 9101) and a polyol ester (ATL 9100), the unlikely assumption was made that all of the used oil consignments were a mixture of these.

Blends of various compositions of ATL 9100 + ATL 9101 were prepared, and their A_{CH_2}/A_{CH_3} ratios determined.

A calibration graph was plotted of % polyol ester vs A_{CH_2}/A_{CH_3} (Fig. 4).

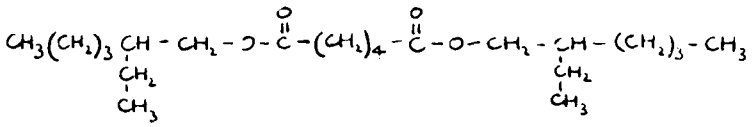
The A_{CH_2}/A_{CH_3} ratio for all of the used oil consignments was determined, and the % polyol ester was read off from the calibration graph.

The results are presented in Table II.

TABLE I

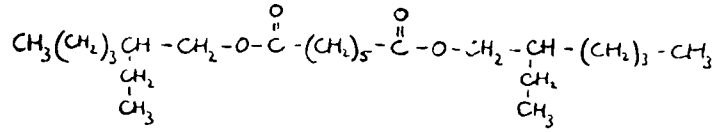
(A). Diesters

Di-(2-ethylhexyl)adipate



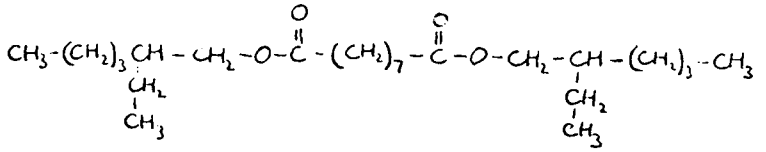
$\frac{CH_2}{CH_3} = \frac{14}{4} = 3.5$

Di-(2-ethylhexyl)pimelate



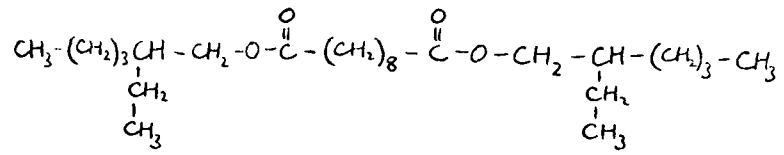
$\frac{CH_2}{CH_3} = \frac{15}{4} = 3.75$

Di-(2-ethylhexyl)azelate



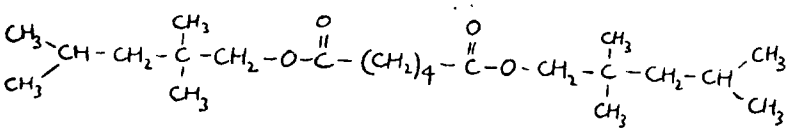
$\frac{CH_2}{CH_3} = \frac{17}{4} = 4.25$

Di-(2-ethylhexyl)sebacate



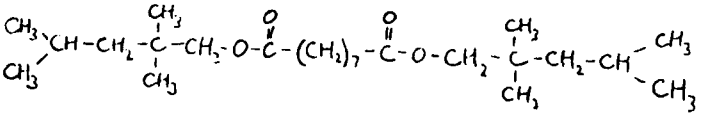
$\frac{CH_2}{CH_3} = \frac{18}{4} = 4.5$

Di-(2,2,4-trimethylpentyl)adipate



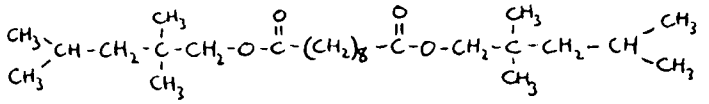
$\frac{CH_2}{CH_3} = \frac{8}{8} = 1$

Di-(2,2,4-trimethylpentyl)azelate



$\frac{CH_2}{CH_3} = \frac{11}{8} = 1.375$

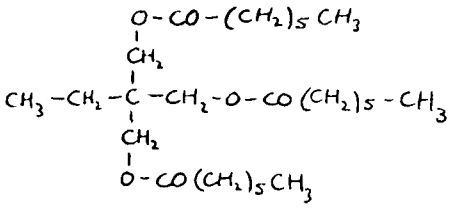
Di-(2,2,4-trimethylpentyl)sebacate



$\frac{CH_2}{CH_3} = \frac{12}{8} = 1.5$

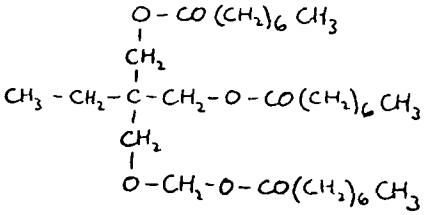
(B) Polyol Esters

Trimethylolpropyl triheptanoate



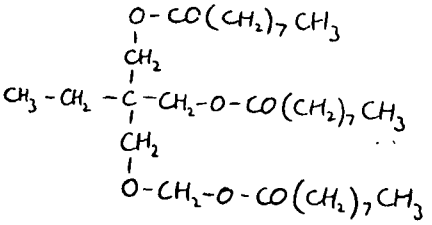
$\frac{CH_2}{CH_3} = \frac{19}{4} = 4.75$

Trimethylolpropyl trioctanoate



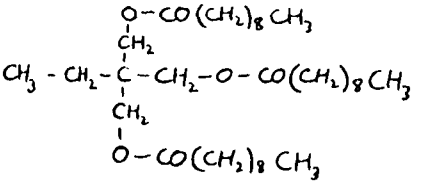
$\frac{CH_2}{CH_3} = \frac{22}{4} = 5.5$

Trimethylolpropyl trinonanoate



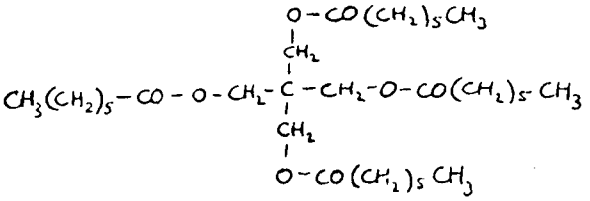
$\frac{CH_2}{CH_3} = \frac{25}{4} = 6.25$

Trimethylolpropyl tridecanoate



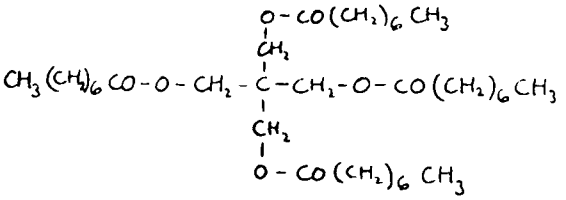
$\frac{CH_2}{CH_3} = \frac{28}{4} = 7$

Pentaerythrityl tetraheptanoate



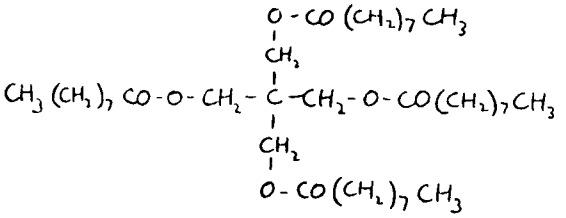
$$\frac{CH_2}{CH_3} = \frac{24}{4} = 6$$

Pentaerythrityl tetraoctanoate



$$\frac{CH_2}{CH_3} = \frac{28}{4} = 7$$

Pentaerythrityl tetrananoate



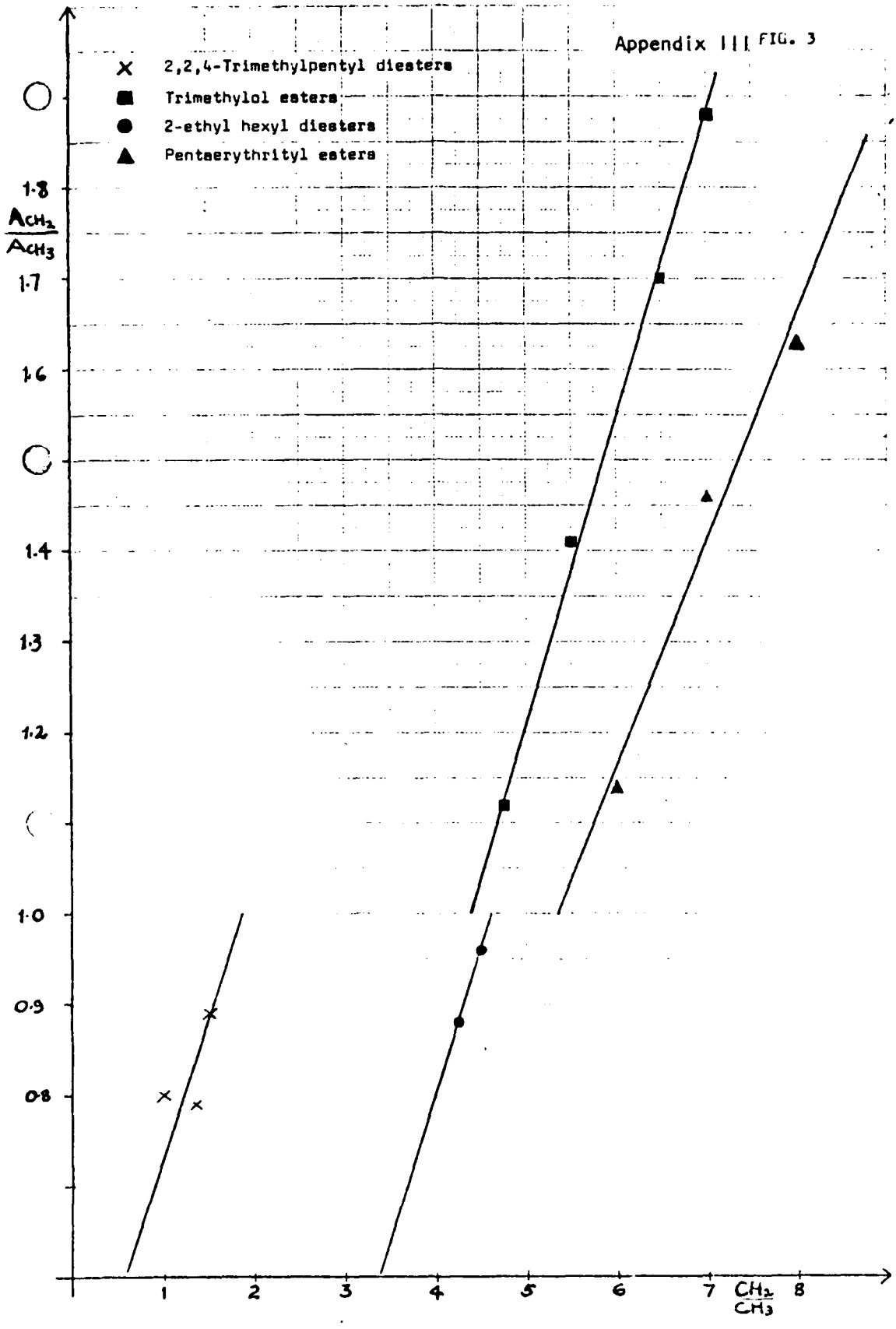
$$\frac{CH_2}{CH_3} = \frac{32}{4} = 8$$

TABLE II

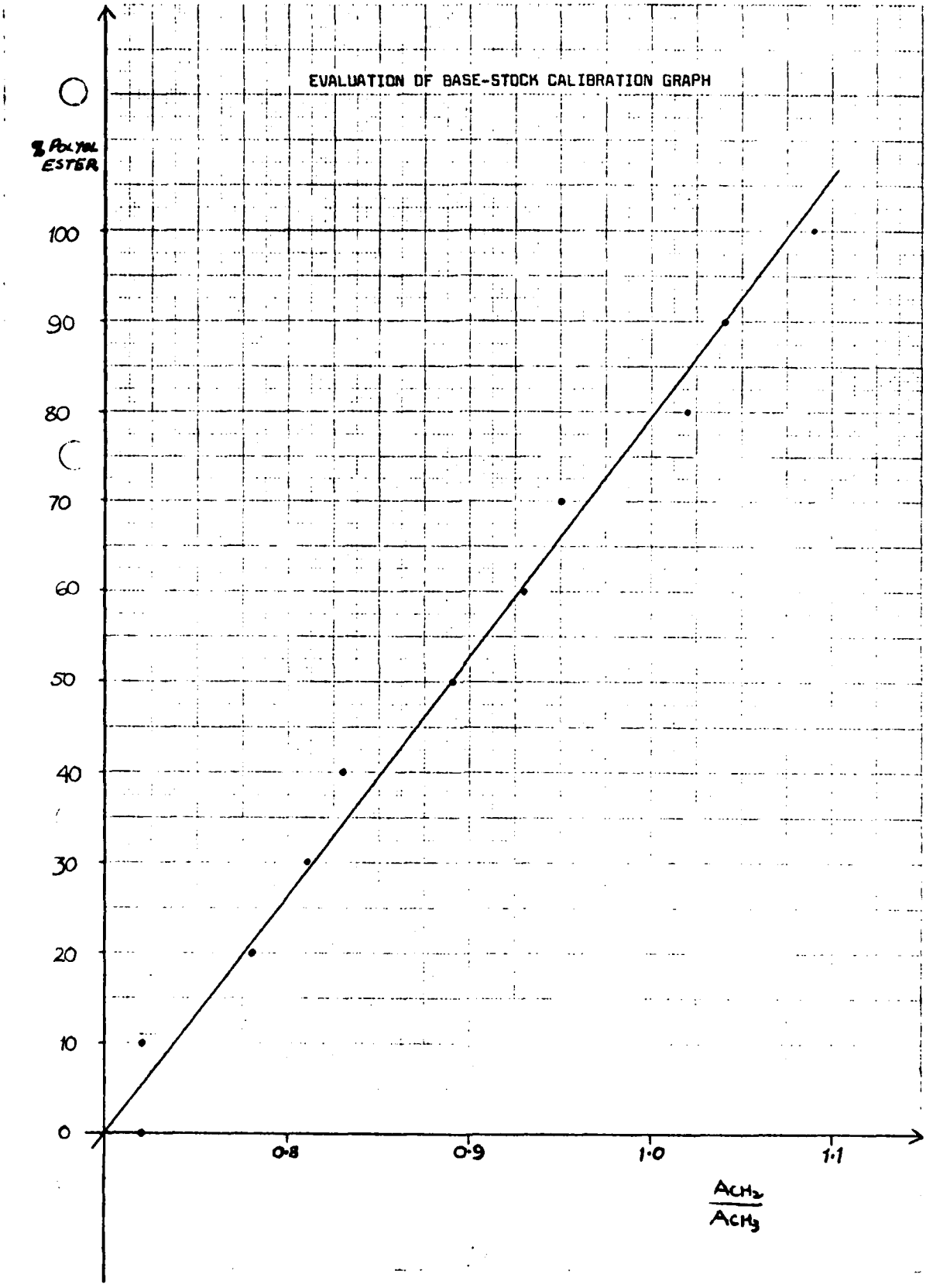
Sample	CH_3			CH_2			$\frac{A_{CH_2}}{A_{CH_3}}$	% POLYOL ESTER *
	Io	I	$\log 10 \frac{Io}{I} = A$	Io	I	$\log 10 \frac{Io}{I} = A$		
D 363	72.8	4.9	1.1719	72.8	4.9	1.1719	1.00	60
D 375	72.8	7.9	0.9645	72.8	6.4	1.0560	1.09	100
D 376	81.0	13.8	0.7686	81.0	12.8	0.8013	1.04	90
D 378	82.2	14.8	0.7446	82.2	13.2	0.7943	1.07	95
D 379	83.0	14.9	0.7459	83.0	14.0	0.7730	1.04	90
D 380	74.5	4.0	1.2701	74.5	3.2	1.3670	1.08	100
D 381	83.0	17.1	0.6861	83.0	16.9	0.6912	1.01	60
D 382	75.5	7.0	1.0328	75.5	7.0	1.0328	1.00	60
D 384	77.8	5.0	1.1920	77.8	5.0	1.1920	1.00	60
D 385	78.5	4.4	1.2514	78.5	3.9	1.3038	1.04	90
D 387	73.8	6.8	1.0356	73.8	6.3	1.0687	1.03	85
D 388	78.2	4.2	1.2700	78.2	4.0	1.2912	1.02	85
D 389	76.8	4.9	1.1952	76.8	5.0	1.1864	0.99	75
D 391	75.5	8.5	0.9465	75.5	8.8	0.9335	0.98	75
D 392	72.0	4.8	1.1761	72.0	4.9	1.1671	0.99	75
D 393	77.2	2.5	1.4897	77.2	2.6	1.4726	0.99	75
D 394	87.0	13.8	0.7996	87.0	14.1	0.7903	0.99	75
D 395	86.0	17.1	0.7015	86.0	17.5	0.6915	0.99	75
D 470	75.0	6.6	1.0555	75.0	9.0	0.9208	0.87	45
D 471	83.5	13.6	0.7882	83.5	15.6	0.7286	0.92	55
D 472	83.0	20.5	0.6073	83.0	21.2	0.5927	0.98	75
D 473	74.9	7.0	1.0294	74.9	8.0	0.9714	0.94	60
D 474	77.2	2.9	1.4252	77.2	4.9	1.1974	0.84	35
D 475	76.9	5.1	1.1784	76.9	6.1	1.1006	0.93	60
D 476	74.0	5.1	1.1617	74.0	6.1	1.0839	0.93	60
D 477	79.5	9.1	0.9413	79.5	10.5	0.8792	0.93	60
D 556	88.8	25.2	0.5470	88.8	24.2	0.5646	1.03	85
D 557	88.3	22.8	0.5880	88.3	21.5	0.6135	1.04	90
D 558	88.7	27.0	0.5166	88.7	24.8	0.5535	1.07	95
D 559	79.2	14.8	0.7285	79.2	13.3	0.7749	1.06	95
D 560	79.5	13.1	0.7831	79.5	12.0	0.8212	1.05	90
D 561	88.0	25.9	0.5312	88.0	24.2	0.5607	1.06	95

* To nearest 5%

Appendix III FIG. 3



Appendix III Fig. 4



APPENDIX IV

HIGH PRESSURE LIQUID CHROMATOGRAPHY (HPLC)

HPLC was used to identify and determine the inhibitors present, both qualitatively, and quantitatively. Various additives were known from past experience and the literature, some of which were used to prepare a standard, comprised of the following:-

1. N-allyl-3,7-dioctylphenothiazine (NADOPT)
2. 4,4'-dioctyldiphenylamine (DODP)
3. N-(4-octylphenyl)-1-naphthylamine (MOPAN)
4. Phenyl-1-naphthylamine (PAN)
5. 3,7-dioctylphenothiazine (DOPT)
6. Phenothiazine (PTZ)

About 1.0000 g of each inhibitor was dissolved in a tetra-ester base-stock (Herculube J), to produce about 100.0000 g oil. 1.0 ml of the standard oil was placed into a 50.0 ml volumetric flask, dissolved in mobile phase, and made up to the mark with the same solvent. Where the determination was especially critical (eg. in quality control of the product) all measurements were carried out by weight.

10 μl of this solution were injected on to the column by means of a Rheodyne valve and 10 μl loop.

The equipment used comprised of an Applied Chromatography Systems pump and UV monitor, together with a Houston Instruments Chart Recorder, and LDC 304 integrator. Columns used were 25 cm x 5 mm with zero dead-volume fittings.

To begin with, a 10 μm silica column was used, together with a mobile phase of hexane and di-isopropyl ether (DIPE). Possessing only an isocratic system, it took many runs to determine the necessary DIPE concentration .

It was found that the increase in polarity of the mobile phase as the DIPE content was increased gave increasingly poorer separation. However, when hexane alone was used, the chromatograms were very poorly resolved with broad peaks. Thus it was eventually decided to use 5% DIPE in hexane, as this was the highest concentration of DIPE (thus giving lower retention times) with which baseline separation was achieved.

A 5 μm silica column was then obtained, which was found to give much better separation of the additives. Thus the conditions finally decided upon were as follows:-

Column:	Spherisorb 5 m silica
Mobile Phase:	5% DIPE in hexane
Detection:	UV @ 254 nm
Flow rate:	1 ml/min

These conditions were then used to determine the additive contents of the unused lubricants received, as well as the used consignments.

PTZ was found to have such a long retention time that it was thought to be impractical to run all the consignments for determination of PTZ content.

However, this problem was resolved later by using a mobile phase of 20% DIPE in hexane. The increased polarity of the mobile phase eluted the PTZ much quicker, and this was used to determine PTZ in the unused oils, as well as D556 thru D561.

Methods were later developed for the determination of benzotriazole (BTZ) and 2-aminobenzamide (ABA).

For BTZ, the following conditions were employed:-

Column: Spherisorb alkylamine 5 μm
Mobile Phase: 100% MeOH
Detection: UV @ 240 nm
Flow Rate: 1 ml/min

Also the conditions for ABA were as follows:-

Column: Spherisorb ODS 10 μm
Mobile Phase: 100% MeOH
Detection: UV @ 254 nm
Flow Rate: 1 ml/min

It was then later found that BTZ could be determined using the ODS column, with 100% MeOH, and UV detection @ 240 nm.

Also additives 1-6 could be determined using this system, but in some cases (eg. DODP and MOPAN) separation was poor, and MeOH was usually found to be an unsuitable solvent for used oils in any case.

An important additive that would have been useful to have been determined was tri-tolylphosphate (TTP). Unfortunately, it was found impossible to develop an analytical method for TTP in the time available, especially with the limited resources and equipment available.

APPENDIX V

Summary of Corrosion Test Procedures

Pretreatment (R.R.1004/Supp.1)

An 85 ml sample occupying approximately 75 per cent of the volume of a closed cylindrical stainless steel vessel (60 mm dia. x 70 mm height) is vented to atmosphere via a 1/16 in. (1.59 mm) hole. The vessel and content are heated in an air-circulating oven for five hours @ 250°C, at the end of which a sample of the pretreated lubricant is subjected to the corrosion test below:-

Corrosion Test (R.R.1002)

Specimens of brass, mild steel, soldered copper, lead, copper, magnesium and aluminium alloys, are mounted on a common stainless steel rod so as to provide continuity of metallic contact. The assembled specimens are totally immersed in 50 ml of the pretreated lubricant for 192 hours @ 150°C. The specimens are of equal area and the ratio of lubricant sample to total metal area is 0.79 ml/cm^2 . Assessment of corrosivity is based upon the changes in weights of the specimens and their appearances at the end of the test period.

APPENDIX VI

SUMMARY OF HYDROLYTIC STABILITY TEST
ROLLS-ROYCE METHOD 1006

250 ml samples of the test lubricant are stored over water in a glass vessel, fitted with a water-trap, and the contents are shaken at specified intervals. Two test runs are carried out, one @ 90°C, and the other @ 70°C, and the hydrolysis at these temperatures is measured in terms of the test durations producing an acidity increase of 1.5 mgKOH/g. The duration over which the acidity increases by this amount @ 40°C is calculated from the 90°C and 70°C results.

APPENDIX VII

SUMMARY OF ROLLS-ROYCE METHOD 1034 - COKING PROPENSITY OF GAS TURBINE LUBRICANTS

0.4 ml of the lubricant sample are introduced, by means of an injector syringe, into a weighed aluminium or stainless steel dish so designed as to ensure uniform thickness of sample over it's internal surface.

The dish and sample are placed in an air circulating oven, maintained at test temperature, for 22 hours at the end of which the dish and resulting residue are cooled in a dessicator for 2 hours and then weighed, the weight of residue being obtained by difference.

These operations are repeated with further 0.4 ml aliquots of the sample which are added to the dish containing the accumulated residues from the preceeding operations until a total of ten cycles in all have been run.

The correlation coefficient showing the degree of relationship between the accumulative residue and the number of cycles is calculated for the ten results, and the expectant residue at the end of 20 cycles is calculated by means of linear regression.

The coking propensity of the lubricant is expressed in terms of milligrams residue produced by 20 cycles at the test temperature, and with the dish material, employed.

APPENDIX VIII

Summary of Rolls Royce Method 1001/Supp. 1 & 2
Oxidative Stability

250 ml/min air, saturated with water vapour, are bubbled under controlled conditions through 50 ml sample at selected temperatures and test durations. After measurement of volatilisation loss, the lubricant sample is topped-up to its original weight with the unblown lubricant, and the levels of degradation, in respect of acidity, viscosity and insoluble matter, are determined.

A series of tests are run to establish effective life at any particular temperature, as defined in SAE Paper No. 690424* in respect of the four modes of degradation.

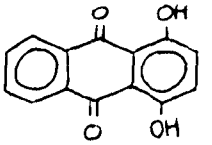
* Edge, R.G., and Squires, ATBP, Lubricant Evaluation and System design for Aircraft Gas Turbine Engines. SAE No. 690424, 69 April 21-24.

Appendix IX

THE DETERMINATION OF 1,4-DIHYDROXYANTHRAQUINONE IN SYNTHETIC GAS TURBINE LUBRICANTS

Introduction

The UV/VIS scan of 1,4-dihydroxyanthraquinone (I) was obtained, and gave rise to the expected peaks in the aromatic region (c.260 nm), as well as some



(I)

absorbance in the 500 nm region.

Using polar solvents such as $CHCl_3$ (Fig. 1) and MeOH (Fig. 2), a broad peak with shoulders was obtained around 500 nm.

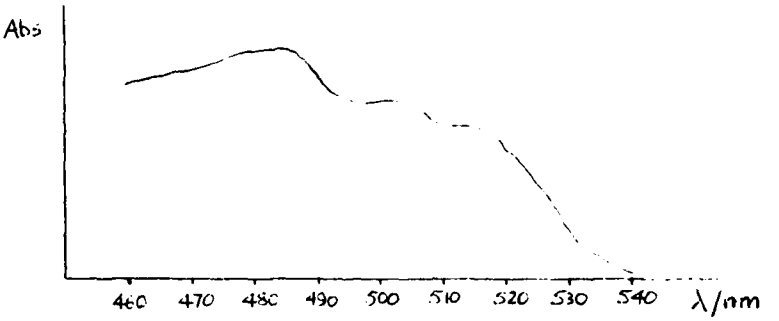


Fig. 1

VIS scan of (I) in $CHCl_3$

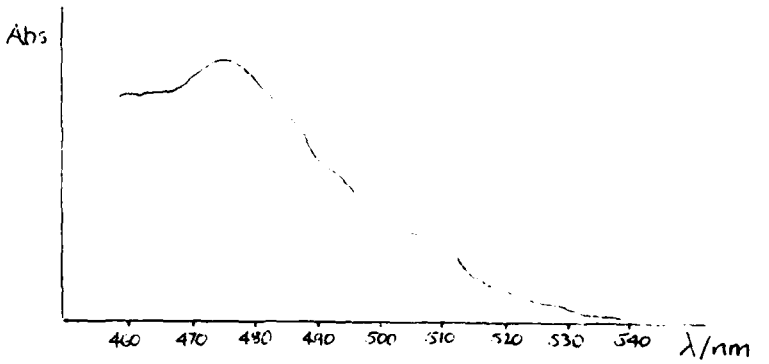


Fig. 2

VIS scan of (I) in MeOH

However, when hexane was used, this broad peak was resolved into a number of peaks, with two distinctive maxima at 507 nm and 518 nm (Fig. 3).

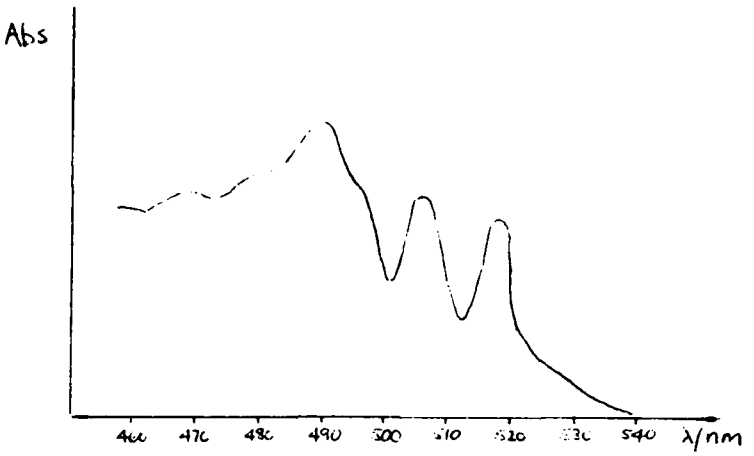


Fig. 3

VIS scan of (I) in hexane

The peak around 518 nm was chosen for the determination.

Experimental

A calibration graph was plotted in the following manner:-

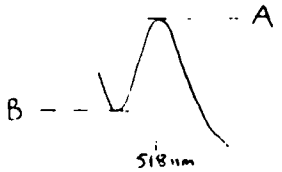
Four oils were prepared by dissolving an accurately determined amount of (I) in di-(2-ethylhexyl) azelate corresponding to 0.2%, 0.1%, 0.05%, 0.025% by weight. 1.0 ml of each oil was pipetted into a 50.0 ml volumetric flask, dissolved in hexane, and made up to the mark with the same solvent, to give solutions A, B, C and D respectively.

The absorbances of solutions A—D were determined at the maximum around 518 nm, by scanning the range 480—540 nm, using a 1.0 ml di-(2-ethylhexyl) azelate solution in 50.0 ml hexane as reference.

The absorbance was plotted against % w/w (I) in the oil (Fig. 4). Also a graph was plotted of % w/w (I) against the peak height of the peak around 518 nm (Fig. 5).

The peak height was determined by subtracting the absorbance of the minimum around 511 nm from the previously determined absorbance (Fig. 6).

Fig. 6



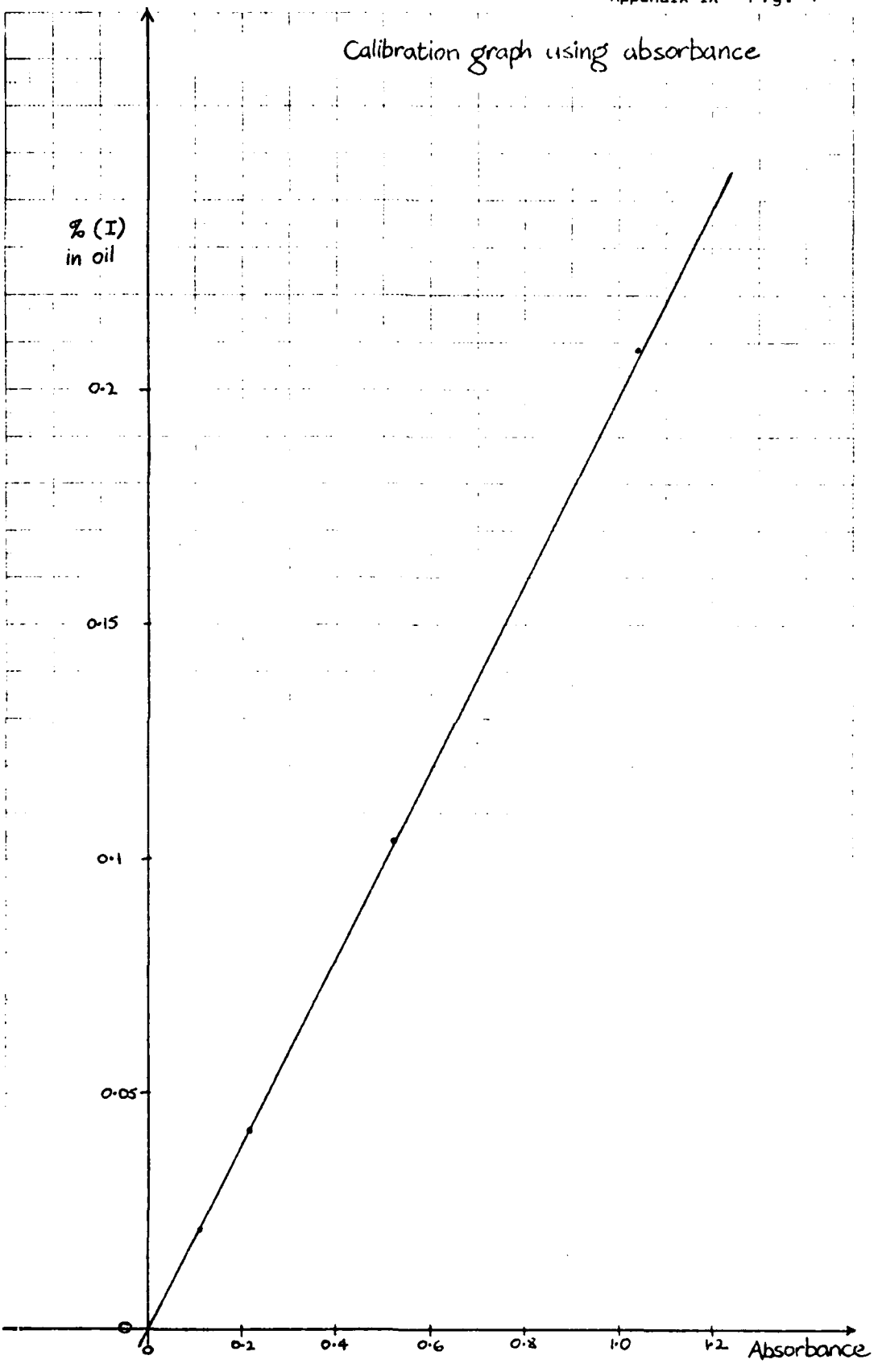
Peak ht.=AbsA - Abs B.

The absorbances and peak heights were then determined for a number of oils, by pipetting 1.0 ml of the oil into a 50.0 ml volumetric flask, dissolving in hexane, and making up to the mark with the same solvent.

The oils used were di-(2-ethylhexyl) azelate containing:-

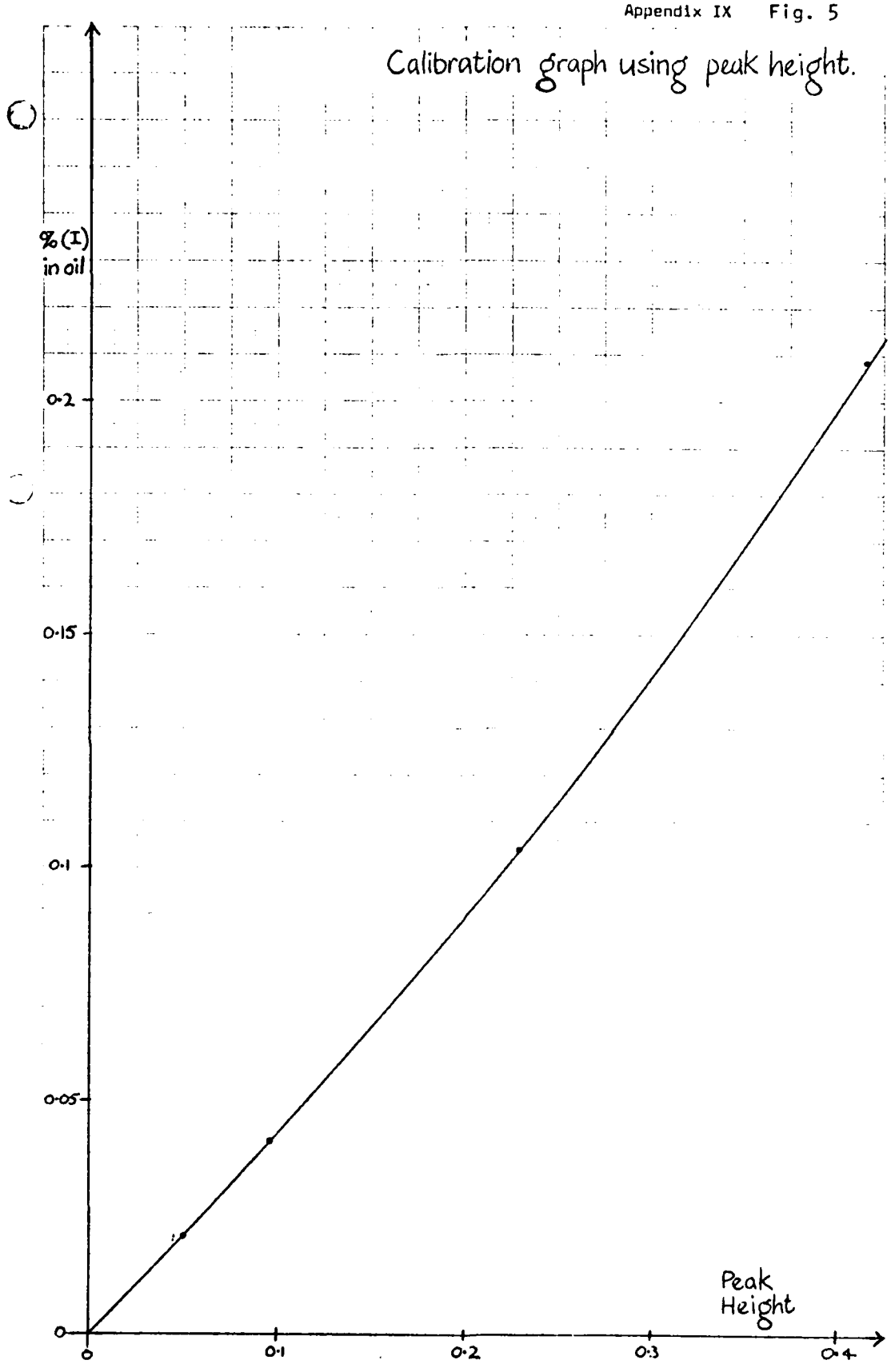
(i) A known amount of (I)
(ii) A known amount of (I) plus 1.5% DODP, 1% MOPAN, 0.5% PAN, 0.5% TPPT, 0.05% BTZ
(iii) A known amount of (I) plus 3.0 DODP, 2% MOPAN, 1% PAN, 0.5% TPPT, 0.05% BTZ

Appendix IX Fig. 4



Appendix IX Fig. 5

Calibration graph using peak height.



Also, a sample of used oil was taken (iv), and after scanning, a known amount of (I) was added to give (v) and the absorbance and peak height again determined.

The % (I) in the oil was then read off both the calibration graphs.

The process was repeated using 1% di-isopropylether in hexane as solvent, since this solvent system is used in HPLC analyses, and the same solution prepared for HPLC may be used to determine (I) by VIS spectroscopy.

Results and Discussion

The determined amounts of (I) in oils (i) — (v) are given in Table 1.

Oil	% (I) Added	% (I) found using absorbance graph	% (I) found using peak height graph
(i)	0.104	0.104	0.105
(ii)	0.050	0.050	0.049
(iii)	0.047	0.050	0.046
(iv)	Nil	0.008	Nil
(v)	0.065	0.070	0.063

TABLE 1

It would seem from these results that there is slightly more error inherent in the peak height graph (presumably since two estimations of absorbance are made), and that more accurate results would be obtained using the absorbance graph, where only (I) is present in an oil, or where other components do not contribute to the absorbance. However, this is very unlikely, and so it would appear that the use of the peak height method effectively eliminates the absorbance due to other components in the oil, and so this should be the method of choice.

The results for the determinations using 1% di-isopropylether in hexane as solvent were identical, thus the solution prepared for HPLC analysis may be used.

The most striking result is the one determined on a used oil. This oil was very dark, and gave an absorbance of 0.045, corresponding to 0.008% of (I). (Fig. 7)

After adding (I), the determination using absorbance graph gave a falsely high value, whereas using the peak height graph gave a value closer to the truth.

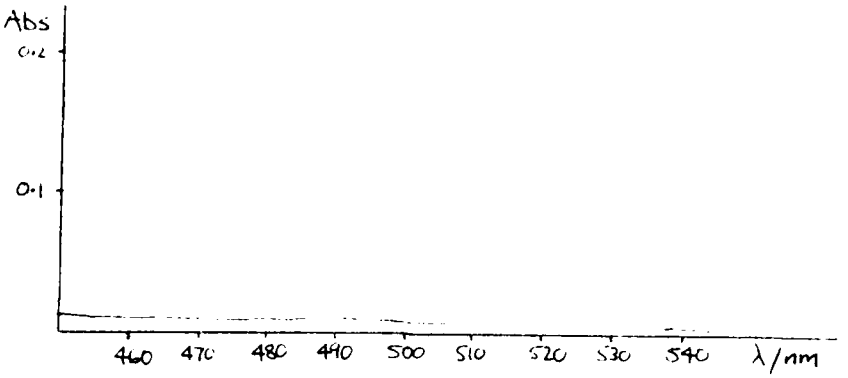


Fig. 7
Vis scan
of (iv)

Conclusion

1,4-dihydroxyanthraquinone may be determined in the presence of other components in a synthetic gas turbine oil by measuring the peak height of the peak around 518 nm, of a solution of the oil in hexane, or 1% di-isopropylether in hexane.

The peak height is determined by subtracting the absorbance at the minimum around 511 nm from that at the maximum around 518 nm.

The value so obtained can then be used to read off directly the % w/w 1,4-dihydroxyanthraquinone in the oil using a calibration curve.

This method is especially useful for determination of 1,4-dihydroxyanthraquinone in used oils, since use of the absorbance calibration curve leads to high results.

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